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Accessing the extent of kerogen/bitumen interactions on source rock maturation and hydrocarbon generation

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Abstract

In order to ascertain whether kerogen and the heavy oil or bitumen generated during the initial stages of source rock maturation then go on to produce similar gas yields compared to the natural situation when they are present in source rocks, a study has been conducted on an immature type II Kimmeridge Clay Formation (KCF) source rock (Dorset, United Kingdom) with different total organic carbon contents (14, 25 and 30 % TOC), and all having an initial vitrinite reflectance (VR) of approx. 0.4 % Ro. Anhydrous and hydrous pyrolysis experiments were conducted on the whole immature source rock, the isolated partially matured bitumen-extracted source rock and the isolated bitumen (bitumen generated and extracted from the initial source rock) and mixtures of the isolated partially matured source rock and bitumen using two types of Hastalloy vessels (22 and 25 ml) at 320-420 °C for 7-48 h over a pressure range of 115-900 bar. Hydrocarbon gas yields and the increase in VR were greater from the whole rock experiments compared to the experiments on the isolated partially matured source rock and isolated bitumen (no mineral matter present), as well as the experiments on mixtures of the isolated partially matured isolated source rock and bitumen combined. The effect of particle size were also found to be of significance as higher gas yields were obtained from recombined mixture experiments using powdered samples (14 % TOC source rocks) compared to using rock chips (30 % TOC source rocks). Hydrocarbon gas yields, pyrobitumen yields, and VR values were found to decrease as pressure increases towards 500 and 900 bar compared to 180 bar at 350 °C where the effects of pressure retardation were found to be much more significant from the partially matured source rock maturation and bitumen in isolation than from the whole source rock. At 420 °C, gas generation, bitumen plus oil and coke yields were not affected by pressure, but VR decreases going from 310 bar to 500 and 900 bar. The results obtained demonstrate that the interplay of inherent mineral matter, reactant phase, source rock/kerogen, bitumen and pressure are key factors in determining the extent of hydrocarbon generation and source rock maturation in geological basins.

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Chapter 1: Introduction and scope of study

Hydrocarbon exploration during the last twenty years has increasingly targeted high pressure deep water geological basins. The geochemical models devised to predict source rock maturity and hydrocarbon generation assume that temperature and geological time are the controlling parameters during hydrocarbon generation and source rock maturation, with pressure having no significant effect (Tissot and Welte, 1984). Most high pressure confined pyrolysis studies using gold bags or capsules as the reaction cell either under anhydrous (absence of water) or hydrous (presence of water) conditions have shown that pressure has minimal (Freund et al., 1993; Michels et al., 1994; Knauss et al., 1997), insignificant (Monthioux et al., 1985 & 1986), enhancing (Tao et al., 2010) or retarding (Hill et al., 1994) effect on hydrocarbon generation and maturation reactions. On the other hand, high pressure hydrous pyrolysis experiments (using fixed volume autoclave reactors) which more closely resemble natural conditions have shown pressure retardation of hydrocarbon generation and source rock maturation (Price 1993; Landais et al., 1994; Michels et al., 1995a & b; Zou and Peng, 2001; Carr et al., 2009) (discussed in detail under Section 2.10).

In geological basins source rock/kerogen, bitumen, and mineral matter are all in close contact, and unavoidably all three components should have a role to play during hydrocarbon generation and maturation reactions. Therefore, mineral matter catalytic effects and the interactions between the reactant phases (source rock/kerogen, bitumen and mineral matter all in intimate contact) should not be overlooked. In addition, water should also play an important role during hydrocarbon generation and organic matter maturation as it is ubiquitous in sediments (Lewan 1985, 1993 & 1997) (discussed in detail in Section 2.9). A considerable amount of work has been undertaken investigating the catalytic effect of minerals using laboratory pyrolysis, and results indicate that hydrocarbon generation and cracking, and source rock maturation were all enhanced in the presence of minerals compared to experiments with no minerals added (Horsfield and Douglas, 1980; Eglinton et al., 1986; Tannenbaum and Kaplan 1985; Tannenbaum

et al., 1986; Huizinga et al., 1987a & b; Pan et al., 2008 & 2010) (discussed in detail in Section 2.11). However, little information is available on the effect of reactant phase (mineral matter, source rock/kerogen, bitumen), and how the presence of bitumen in source rock can influence hydrocarbon gas generation and source rock maturation. This study aims to address these issues, as well as investigating the influence of high water pressure on hydrocarbon gas generation and source rock maturation from the bitumen cracking and source rock maturation in isolation.

To do this, bitumen was first generated from the immature type II Kimmeridge Clay Formation (KCF) source rock of different total organic carbon contents (14, 25 and 30 % TOC) and then extracted from the partially matured source rock. The conditions used for the bitumen generation experiments were selected so as to avoid the onset of bitumen cracking to oil. This enabled the partially matured bitumen-extracted source rock and the corresponding bitumen to be pyrolysed individually and in recombined mixtures (partially matured source rock mixed with corresponding extracted bitumen) at higher temperatures. The summation of gas (C_1-C_4), liquid (bitumen plus oil), and solid (residual rock and coke) product contributed from the bitumen generation experiments, isolated partially matured rock and bitumen experiment, and recombined mixture experiments will be compared with the results from those on the whole rock experiments, where source rock, mineral matter and bitumen are not separated. In addition, the results will also be compared to an experiment conducted with larger particle size Kimmeridge Clay Formation (KCF) source rock. The comparative study will be conducted in order to ascertain the effects of reactant phase (mineral matter, source rock/kerogen and bitumen all in close contact), high water pressure and effects of particle size on hydrocarbon gas generation and source rock maturation.

Chapter 2: Literature review

2.1. Kerogen.

Kerogen is termed as the insoluble macromolecular material comprising mixtures of macerals and reconstituted degradation products of organic matter (Tissot and Welte, 1984; Durand, 2003; Killops and Killops, 2005). With increased burial depth and subsequent temperature increase, the thermodynamically unstable kerogen is decomposed and transformed by means of a complex network of reactions into increasingly more stable compounds (Tissot and Welte, 1984; Hoering, 1984; Durand, 2003; Killops and Killops, 2005; Erdmann and Horsfield, 2006; Vandenbroucke and Largeau, 2007). Kerogens typically contain carbon, hydrogen and oxygen elements where for every 1000 carbon atoms, there are around 500-1800 hydrogen atoms, 25-300 oxygen atoms, 5-30 sulphur atoms and 10-35 nitrogen atoms (Killops and Killops, 2005; Vandenbroucke and Largeau, 2007). The composition of the kerogen is dependent on the initial input of organic matter and the nature and extent of microbial activity in the upper sedimentary layers during diagenesis. Consequently, they can be classified into four types namely; Type I, Type II, Type III and Type IV (or residual kerogen) (Tissot and Welte, 1984; Behar and Vandenbroucke, 1987; Durand, 2003; Peters et al., 2005; Killops and Killops, 2005).

2.1.1. Type I kerogen.

This rare kerogen is proposed to be derived from algal lipids (fresh water alga botryococcus braunii) or organic matter enriched in lipids via microbial activity (Killops and Killops, 2005). It is formed in relatively fine-grained, organic-rich, and anoxic muds that are deposited in quiet, oxygen-deficient, shallow water environments such as lagoons and lakes (Tissot and Welte, 1984; Behar and Vandenbroucke, 1987; Speight, 1999; Durand, 2003; Peters et al., 2005; Killops and Killops, 2005). Type I (liptinite-type) kerogen contains extensive aliphatic chains ($\geq C_{40}$) which are mainly derived from alga lipids and algaenan, few aromatic units and heteroatoms. When compared to other

types of kerogen, the amount of oxygen is small and is available in the form of ether groups (Tissot and Welte, 1984; Behar and Vandenbroucke, 1987; Killops and Killops, 2005). It has a high H/C ratio (≥ 1.5), a low O/C ratio (< 0.1) and a high Rock Eval HI (> 600 mg/g TOC), resulting in a high potential for oil (usually paraffinic) and hydrocarbon gas production. Oil generation from type I kerogen can occur at higher maturities due to the predominant C-C bonds being the strongest among the kerogen types (Peters et al., 2005; Killops and Killops, 2005; Vandenbroucke and Largeau, 2007).

2.1.2. Type II kerogen.

The organic matter in type II kerogen is usually derived from mixtures of phytoplankton, zooplankton and micro-organisms that were deposited in a reducing environment. Type II kerogens have a slightly lower Rock Eval HI (300-600 mg/g TOC) and atomic H/C ratios, but higher O/C ratios than type I kerogens (Tissot and Welte, 1984; Peters et al., 2005; Killops and Killops, 2005). Type II (exinite-type) kerogen contains a significant amount of polyaromatic nuclei, heteroatomic ketones, carboxylic acid groups and ester bonds (Tissot and Welte, 1984; Speight, 1999; Killops and Killops, 2005). The saturated material in type II kerogen comprises abundant naphthenic rings and aliphatic chains of moderate length (≤ C_{25}) (Killops and Killops, 2005; Vandenbroucke and Largeau, 2007). Type II kerogens can also be classified as type II-S kerogen, which are rich in sulphur (8-14 % organic sulphur by weight). Despite having a lower oil generating potential than type I kerogens, type II kerogens are considered as a primary source of hydrocarbons in various oil and gas fields (Tissot and Welte, 1984; Speight, 1999; Peters et al., 2005; Killops and Killops, 2005). An example of a Type II-S kerogen is the Kimmeridge Clay from Dorset U.K investigated in this study.

2.1.3. Type III kerogen.

Type III kerogens are derived from woody terrestrial material consisting of a few long chains ($\geq C_{25}$) originating from higher plant waxes (lipinites), cutin (exinites), and some chains of medium length (C_{15} to C_{20}) from vegetable fats, methyl groups and other short chains (Tissot and Welte, 1984; Speight, 1999; Killops and Killops, 2005). Type III (vitrinite-type) kerogens also contains significant amounts of condensed polyaromatic and heteroaromatic ketones and carboxylic acid groups with a small amount of ester groups (Tissot and Welte, 1984; Speight, 1999; Killops and Killops, 2005; Vandenbroucke and Largeau, 2007). They have a relatively low initial H/C ratio (< 1.0), a high initial O/C atomic ratio (as high as 0.3) and a low Rock Eval HI (50-200 mg/g TOC). Type III kerogen is comparatively less favourable for oil generation than types I or II, although it may be a source of gas in source rocks (primarily methane) at sufficient depths (Tissot and Welte, 1984; Speight, 1999; Peters et al., 2005; Killops and Killops, 2005; Vandenbroucke and Largeau, 2007).

2.1.4. Type IV kerogen.

Type IV kerogen is reported to be formed from a higher plant matter that has been severely oxidized on land and then transported to its deposition site (marine or non marine conditions), or intertinitic material originating from subareal weathering or biological oxidation (Tissot and Welte, 1984; Killops and Killops, 2005). Type IV kerogen (residual kerogen) primarily comprises a black opaque debris largely composed of carbon in the form of inertinite and abundant aromatic nuclei and oxygen containing groups in the absence of aliphatic chains. It exhibits a very low H/C ratio (< 0.8) and a high O/C ratio and is incapable of generating hydrocarbons. It is considered as a form of “dead carbon” in the sense of petroleum generation; however they have also been regarded principally as gas producers with much less oil potential than type I to type III kerogens (Tissot and Welte, 1984; Speight, 1999; Peters et al., 2005; Killops and Killops, 2005).

2.2. Organic matter maturation.

As sediments are buried, kerogen undergoes thermal cracking which leads to petroleum generation. With increased burial depth and subsequent temperature increase, these kerogens can undergo three successive stages of maturation, namely: diagenesis, catagenesis and metagenesis (Hoering, 1984; Behar and Vandenbroucke, 1987; Durand, 2003; Killops and Killops, 2005; Vandenbroucke and Largeau, 2007).

2.2.1. Diagenesis.

Diagenesis refers to the biological, physical and chemical alteration of organic matter in sediments prior to significant changes caused by heat (Durand, 2003; Killops and Killops, 2005; Vandenbroucke and Largeau, 2007). Diagenesis begins in recently deposited sediments (first ten or hundred meters of sediment) where the first stage of kerogen alteration and transformation of the organic matter occurs via microbial (biological) activity (Tissot and Welte, 1984; Durand, 2003; Killops and Killops, 2005; Vandenbroucke and Largeau, 2007). Other than the biological transformations, chemical transformations and possible catalysis by minerals surfaces are also possible (Mcnab et al., 1952; Tissot and Welte, 1984). Under considerable time and depth, heteroatomic bonds in the kerogen are progressively broken with the elimination of oxygen resulting in CO_2 and H_2O formation. The first petroleum products liberated by these transformations include mostly heteroatomic (N, S O) compounds of high molecular weight especially asphaltenes and resins (Tissot and Welte, 1984; Hoering, 1984; Durand, 2003; Killops and Killops, 2005; Vandenbroucke and Largeau, 2007).

2.2.2. Catagenesis.

Catagenesis is the process by which the organic matter in rocks is thermally altered during burial over millions of years (Peters et al., 2005) between temperatures of 60 to 100 °C (Killops and Killops, 2005). As temperature increases, different chemical bonds (ester and some C-C bonds) in kerogen and previously generated N, S, O compounds are

broken, resulting in the release of hydrocarbons molecules, specifically aliphatic chains (Tissot and Welte, 1984; Killops and Killops, 2005; Vandenbroucke and Largeau, 2007). At this stage of catagenesis, the main zone of oil generation is accompanied by the formation of a significant amount of gas is believed to occur (Tissot and Welte, 1984; Durand, 2003; Killops and Killops, 2005; Vandenbroucke and Largeau, 2007). The new hydrocarbons generated at this stage have a medium to low molecular weight with no particular structure or specific distribution (Tissot and Welte, 1984; Killops and Killops, 2005). The stage of condensate and wet gas formations are also reached during catagenesis, due to the increasing burial depth and temperature causing more frequent breaking of carbon-carbon bonds in the already formed source rock hydrocarbons and the remaining kerogen (Tissot and Welte, 1984; Killops and Killops, 2005). Further cracking will lead to a significant formation of methane and the lighter hydrocarbons in the source rock and petroleum. Between 60 to 150 °C, oil and C_{2+} hydrocarbon gases are believed to formed, which has been termed as the 'oil window'. The cracking of liquid oil is believed to begin at a temperature of about 150 °C which is comparable to a burial depth of about 5000 m depending on the geothermal gradient (Tissot and Welte, 1984; Killops and Killops, 2005).

2.2.3. Metagenesis.

Metagenesis (also termed as metamorphism) is the final stage of organic matter evolution occurring at great depths. It is the process whereby the remaining kerogen has lost a large part of its hydrogen and has undergone aromatization and some structural rearrangement. The source rock hydrocarbons and reservoir petroleum oil are possibly cracked at these depths to gas temperatures of 150 to 500 °C, resulting in no liquid hydrocarbons and formation of large amounts of methane and a carbon residue named pyrobitumen (Evans et al., 1971; Tissot and Welte, 1984; Behar and Vandenbroucke, 1987; Peters and Moldowan, 1993; Speight, 1999; Durand, 2003; Killops and Killops, 2005; Vandenbroucke and Largeau, 2007).

2.3. Reaction path of kerogen during hydrocarbon generation.

Many studies have described that the formation of petroleum follows the reaction path: Kerogen → Bitumen → Gas + Oil + Residue (Tissot and Welte, 1984; Speight, 1999; Durand, 2003; Killops and Killops, 2005). Lewan (1985) simulated the stages of petroleum generation via hydrous pyrolysis showing that when kerogen is thermally decomposed, it firstly results in the formation of bitumen and minor amounts of expelled oil, and further thermal decomposition of the bitumen leads to the primary generation of expelled oil. Several authors also provide evidence via Rock Eval and micro-scaled sealed pyrolysis (where these open system pyrolysis are used to simulate gas generation from kerogen and polar bitumen), and confined pyrolysis (where these closed system pyrolysis are used to simulate gas generation from oil cracking) that bitumen always represents a short-lived transient phase in the cracking reaction pathway linking kerogen and oil (Ungerer and Pelet, 1987; Dieckmann et al., 1998 & 2000; Erdmann and Horsfield, 2006). Furthermore, they indicate that the source of the gas is not part of the original kerogen but from a thermally stable bitumen which forms at relatively low levels of maturation via recombination reactions involving the liquid products cogenerated with primary gas. The cracking of highly stable substituents from the recombined bitumen is the main gas-forming pathway for a type II organic matter. Erdmann and Horsfield (2006) describes that during progressive burial depth of the source rocks in geologic basins or during increased temperatures in laboratory pyrolysis experiments, the conversion of kerogen into thermogenic hydrocarbons (bitumen, oil, gas, and residue) can be organized into three overlapping stages described below:

$$\text{Kerogen (K)} \rightarrow \text{Coke}^{K} + \text{Bitumen (B)} + \text{Gas}^{K} \qquad (1)$$

$$\text{Bitumen (B)} \rightarrow \text{Coke}^{B} + \text{Oil (O)} + \text{Gas}^{B} \qquad (2)$$

$$\text{Oil (O)} \rightarrow \text{Coke}^{O} + \text{Gas}^{O} \qquad (3)$$

Where K is the mass of kerogen, B is the mass of bitumen and O is the mass of cracked oil.

During thermal alteration, the kerogen first forms thermally stable bitumen (stage 1) at relatively low levels of maturation via recombination reactions, before it is cracked to oil (stage 2). The primary (Gas^{K} + Gas^{B}) and secondary (Gas^{O}) hydrocarbon gases are generated directly from macromolecular precursors (kerogen and polar bitumen) and oil cracking (stage 3), respectively (Ungerer and Pelet, 1987; Dieckmann et al., 1998 & 2000; Erdmann and Horsfield, 2006). The cracking of highly stable substituents from the recombined bitumen, via the alpha cleavage of methyl groups, is the main gas-forming pathway for this type of organic matter. During stages 1, 2 and 3, cyclization also occurs in the residue, and the small number of polyaromatic nuclei, which are left, can undergo reorientation. The resulting structure is formed of quasi parallel layers of aromatic condensed rings, fairly similar to that of graphite (Behar and Vandenbroucke, 1987; Michels et al., 1995b; Erdmann and Horsfield, 2006).

2.4. Constituents in petroleum.

Petroleum is termed as a complex mixture of naturally occurring hydrocarbons containing nitrogen, sulphur and oxygen compounds (usually termed collectively as polar NSO compounds) and traces of various metals such as nickel and vanadium (Speight, 1999; Killops and Killops, 2005). Depending on the nature, the proportion of the compounds it is constituted, and the surrounding temperature and pressure, petroleum can occur in three different forms; natural gas (mainly gaseous hydrocarbons as well as carbon dioxide), liquid (normally termed as crude oil and contains a very wide range of hydrocarbon compounds) and solid (bitumen containing the heaviest and most complex hydrocarbon compounds). The average composition of petroleum by weight usually contains 57 % aliphatic hydrocarbons, 29 % aromatic hydrocarbons and 14 % resin and asphaltenes (Tissot and Welte, 1984; Speight, 1999; Killops and Killops, 2005).

It has been considered by Bestougeff (1967) that aliphatic and aromatic hydrocarbons are the principal type of hydrocarbons. Aliphatic hydrocarbons (also known as saturates or paraffins) are divided into acyclic alkanes (normal and branched) and cycloalkanes (cycloparaffins or naphthenes) (Peters at al., 1990; Killops and Killops, 2005; Peters et al., 2005). They are usually abundant in crude oils, comprising around 60 % of paraffinic-napthenic crude oils, 40-45 % of aromatic crude oils and 20-25 % of degraded heavy oils and tars that have lost part or all their alkanes (Tissot and Welte, 1984; Killops and Killops, 2005).

Aromatic hydrocarbons are hydrocarbons with structures containing benzene rings side chains and aliphatic bridges and may be distinguished as mono-, di-, tri- and poly-aromatics (PAH) (Peters at al., 1990). Aromatic hydrocarbons include pure aromatics, cycloalkanoaromatics or napththenoaromatics molecules, cyclic sulphur compounds and NSO compounds (Tissot and Welte, 1984). An example of a cycloalkane aliphatic hydrocarbon (C_{27} Diacholestane) and an aromatic compound (Ring-C Monoaromatic steroid $C_{27}H_{42}$) are shown in Figures 2.1 and 2.2, respectively (Peters et al., 2005).

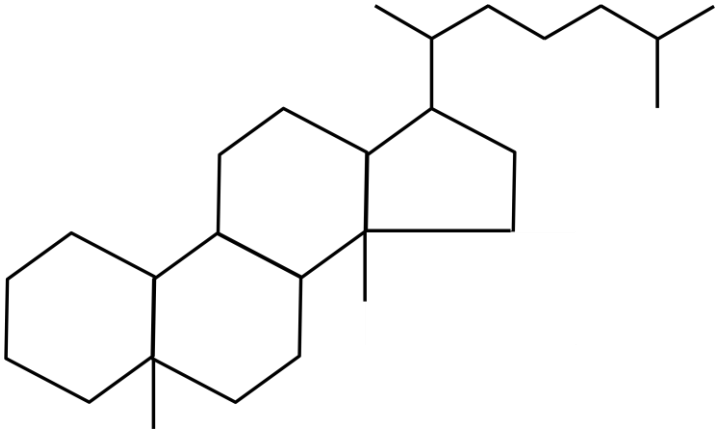


Fig. 2.1. Molecular structure of C_{27} Diacholestane (Peters et al., 2005)

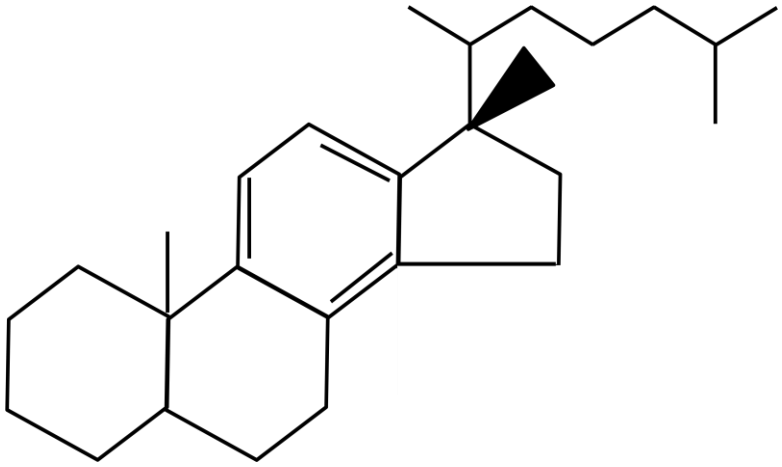


Fig. 2.2. Ring-C Monoaromatic steroid $C_{27}H_{42}$ (Peters et al., 2005)

2.4.1. Bitumen.

Bitumen consists of solid or liquid hydrocarbons and other organic compounds that can be extracted from fine-grained sedimentary rocks using organic solvents such as carbon disulphide or dichloromethane (Killops and Killops, 2005; Peters et al., 2005; Carr et al., 2009). It comprises three main fractions namely; asphaltenes, resins and hydrocarbons (Tissot and Welte, 1984, Killops and Killops, 2005). Asphaltenes and resins are heavy N, S, O containing molecule and are the higher molecular polycyclic fractions constituents of bitumen and crude oils, while the hydrocarbons are usually of lower molecular weights (Czarnecka and Gillott, 1980; Tissot and Welte, 1984). Resins and asphaltenes are usually distinguished by their separation procedures (Tissot and Welte, 1984). Asphaltenes precipitate from crude oil when a large quantity of low-molecular-weight alkanes is added (such as *n*-pentane), while resins (polars) remain in solution (Peters et al., 2005). Both resins and asphaltenes comprises around 0-40 % of non-degraded crude oils, depending on genetic type and thermal maturity. They are usually in high concentration in shallow immature petroleum and decreases with increasing depth and subsequent cracking (25-60 %) due to microbial activity, water washing and oxidation (Tissot and Welte, 1984; Speight, 1999). Killops and Killops (2005) suggested that bitumen is formed during the diagenesis stage at the expense of kerogen, where the heteroatomic bonds are broken successively and roughly in order of ascending rupture energy, starting with some labile carbonyl and carboxyl groups (like ketones and acids). The formation of bitumen is an intermediate to kerogen decomposition and oil generation involving the breaking of weak bonds within the kerogen (Lewan, 1997; Erdmann and Horsfield, 2006). Bitumen is frequently found filling pores and crevices of sandstone, limestone or argillaceous sediments, in which case the organic and associated mineral matrix is known as rock asphalt (Tissot and Welte, 1984; Speight, 1999; Killops and Killops, 2005).

Lewan (1992) has developed a working hypothesis describing the reaction pathways involving a bitumen molecule. He describes that a bitumen molecule can be subjected to a barrage of extraneous free radicals thermally generated from other bitumen molecules

or from the kerogen. The free radical fragments and free radical sites formed on the bitumen molecule can be frequently terminated with water derived hydrogen resulting in the formation of liquid oil and by recombination with other free radical sites on the bitumen or neighbouring molecular fragments resulting in the formation of pyrobitumen coke (Behar and Vandenbroucke, 1987; Lewan, 1992; Michels et al., 1995b; Erdmann and Horsfield, 2006). Figure 2.3 shows a proposed chemical structure of asphaltene present in bitumen.

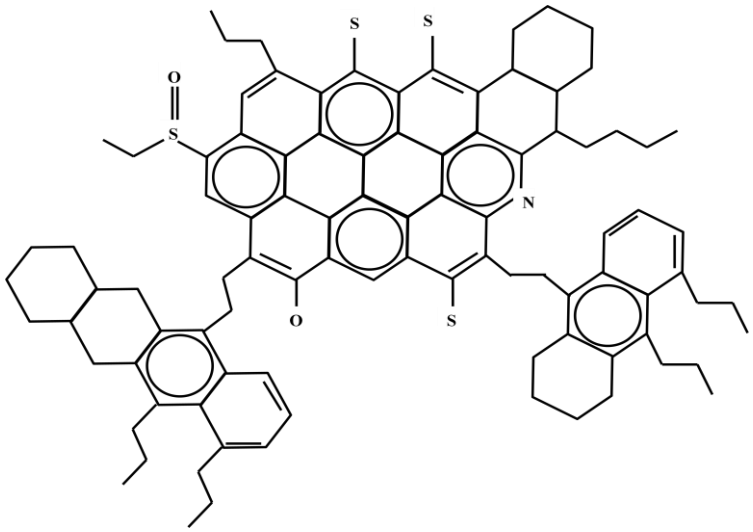


Fig. 2.3. Proposed molecular structure of asphaltene in bitumen (Sayyad Amin et al., 2011).

2.4.2. Pyrobitumen.

Coke or insoluble pyrobitumen is the solid carbonaceous material produced from petroleum by aromatization and ring condensation reactions during thermal processing. It is often distinguished by having a high carbon content (usually 95 % by weight) and a honeycomb type of appearance. The colour varies from gray to black, and the material is insoluble in organic solvents (Tissot and Welte, 1984; Hill et al., 1996; Speight, 1999; Killops and Killops, 2005).

2.5. Petroleum alterations in geological basins.

After oil is pooled, several processes are capable of drastically altering its composition. Some of the most common alteration processes are thermal alteration, deasphalting, biodegradation and water washing (Evans et al., 1971; Tissot and Welte, 1984; Killops and Killlops, 2005). Thermal alteration of petroleum proceeds under the influence of heat in the subsurface, depending on the depth of the reservoir and subsequent geothermal gradient (Tissot and Welte, 1984; Killops and Killops, 2005). Oil becomes susceptible to thermal cracking with increasing depth of burial and time of residence at temperatures above 160-200 °C (Tissot and Welte, 1984; Killops and Killops, 2005). As temperature increases, reservoir oil composition becomes specifically light with a linear increase in low molecular weight hydrocarbons (< C_{15} carbon atoms) at the expense of high molecular weight hydrocarbons (> C_{15} carbon atoms) (Tissot and Welte, 1984).

Deasphalting refers to the natural precipitation of asphaltenes from heavy to medium crude oils due to the presence of large amount of gas and light hydrocarbons in the range from C_1-C_6 (Tissot and Welte, 1984). Deasphalting can occur due to large amount of hydrocarbon gas generated by thermal maturation in a reservoir or injection of externally generated hydrocarbon gas or light oil during secondary migration (Tissot and Welte, 1984; Killops and Killops, 2005).

Water washing refers to the removal of lighter and water soluble hydrocarbons from crude oils, by the flow of subsurface formation waters under saturated with hydrocarbons moving along the oil-water interface in a reservoir (Tissot and Welte, 1984; Killops and Killops, 2005). The susceptibility of individual hydrocarbons to water washing depends on their solubility where the most susceptible components include polar compounds and smaller hydrocarbons (Killops and Killops, 2005). Lighter hydrocarbons are more affected than heavier hydrocarbons and light aromatics more than branched and cyclic paraffins, while heavy normal paraffins are least affected Tissot and Welte, 1984; Killops and Killops, 2005).

Biodegradation is the microbial alteration of crude oil, by selective utilization of certain types of hydrocarbons by micro-organisms, leading to the formation of heavier oil (Tissot and Welte, 1984). It can be classified as aerobic (caused by aerobic bacteria) or anaerobic (caused by anaerobic bacteria) (Larter et al., 1996; Wilkes et al., 2000) Aerobic biodegradation occur when bacteria are introduced into an oil pool with oxygen rich meteoric waters, the bacteria apparently utilize this dissolved oxygen and metabolize preferentially certain types of hydrocarbons (Tissot and Welte, 1984). In anaerobic biodegradation, the oxygen supply of bacteria is probably derived from dissolved sulphate ions (Tissot and Welte, 1984). The non hydrocarbon contents of crude oils particularly asphaltenes increases with biodegradation (Bailey et al., 1973a & b). According to the studies conducted by (Wilkes et al., 2000; Peters et al., 2005), the different types oil constituents are degrades sequentially; *n*-alkanes > mono-cyclc alkanes > alkylbenzenes > isoprenoid alkanes > alkylnaphtalenes > bicyclic alkanes > steranes > hopanes > diasteranes > aromatic steroids > porphyrins. Alteration of reservoir petroleum affects the composition of crude oil, which tends to obscure the original character of the oil, and therefore affects crude oil correlation studies, and influences the quality and economic value of petroleum (Tissot and Welte, 1984).

2.6. Maturity indicators for source rocks.

Thermal evolution of organic matter in source rocks changes many physical or chemical properties of the organic matter, where these properties can be considered as indicators for maturation (Tissot and Welte, 1984). Various thermal maturity parameters have been developed by organic geochemists, but for the purpose of this study, organic matter maturity parameters that will be discussed include vitrinite reflectance and biological markers (Section 2.7) only (Tissot and Welte, 1984; Price and Wenger, 1992; Peters and Moldowan, 1993; Landais et al., 1994; Michels et al., 1995b; Peters et al., 2005).

Vitrinite reflectance is the measurement of reflectance of the vitrinite coal macerals under monochromatic light (Tissot and Welte, 1984; Killops and Killops, 2005). It is widely accepted by exploration geologists as a key measure of the thermal maturity (Peters et al., 2005) such as measuring the rank of coals, or can be applied in assessing thermal maturity of types II and types III kerogens (Tissot and Welte, 1984; Killops and Killops, 2005). Reflectance measurement is usually made on the isolated macerals of the kerogen, which is immersed in oil to prevent stray reflections when illuminated with the monochromatic light (Peters et al., 2005; Killops and Killops, 2005). Vitrinite reflectance values are usually expressed as a percentage by the term % Ro. Thermal maturation causes vitrinite to become more aromatized and reflective. The increase in reflectance of vitrinite caused by the increase of planar aromatic sheets in the kerogen/coal structure continues throughout thermal oil generation. Hence, it can be used as an indicator of the thermal stress experienced by the organic matter (Tissot and Welte, 1984; Behar et al., 2003; Peters et al., 2005). It is reported by various studies that the correlation of vitrinite reflectance can be correlated to the stages of oil generation for different types of kerogen (Tissot and Welte, 1984; Behar et al., 2003; Peters et al., 2005). Vitrinite reflectance values of Ro < 0.5 to 0.7 % can be interpreted as the diagenesis stage (source rock is immature); Ro of 0.7 to 1.3 % and 1.3 to 2.0 % corresponds to catagenesis stage during main zone of oil generation or oil window and zone of wet gas and condensate, respectively; whereas Ro > 2.0 % corresponds to metagenesis stage (dry gas zone) where methane remains as the only hydrocarbon (Tissot and Welte, 1984; Peters et al., 2005; Killops and Killops, 2005).

Other maturity parameters to be considered are transformation ratio, temperature index (T_{max}) and hydrogen index (HI) via Rock Eval pyrolysis, fluorescence technique and biological markers (Tissot and Welte, 1984; Price and Wenger, 1992; Landais et al., 1994; Michels et al., 1995b; Peters et al., 2005). The transformation ratio is expressed by the $S_1/(S_1+S_2)$, which increases with increasing maturity (Tissot and Welte, 1984; Peters et al., 2005). S_1 represents the amount of free hydrocarbons (oil and gas) already present in the sample and are distilled out during Rock Eval pyrolysis at initial heating temperatures of 350 °C; whereas S_2 represents the amount of hydrocarbons generated through thermal cracking of the non volatile organic matter (kerogen) at temperatures of 550 °C. T_{max} is the peak temperature corresponding to the maximum of S_2 hydrocarbon generation during Rock Eval pyrolysis which reflects the increasing thermal energy required to break the remaining bonds in kerogen associated with hydrocarbon generation. The value of T_{max} increases with increasing maturity (Tissot and Welte, 1984; Peters et al., 2005; Killops and Killops, 2005). Hydrogen index is expressed by the ratio S_2/TOC in mg/g, and is used for both source rock characterization and maturity assessment which decreases with increasing maturity (Price and Wenger, 1992; Landais et al., 1994; Michels et al., 1995b; Behar et al., 2003; Peters et al., 2005). Rock Eval T_{max} and transformation ratio less than 435 °C and 0.1, respectively, indicate immature organic matter that generated little or no petroleum. The transformation ratio reaches 0.4 at the bottom of the oil window (beginning of the wet gas zone) and can increase to as high as 1.0 when the hydrocarbon-generative capacity of the kerogen has been exhausted (Peters et al., 2005). Fluorescence is an optical maturity parameter where lipinite constituents is induced by blue or UV light (Tissot and Welte, 1984). Lipinite maceral fluorescence under the blue or UV light, where the intensity and wavelength of the fluorescence is used as a maturity indicator (Killops and Killops, 2005). Fluorescence is intense in shallow immature samples and decreases during diagenesis and most catagenesis, and at the end of oil zone it has usually completely disappeared (Tissot and Welte, 1984).

2.7. Biological markers.

Biomarkers are complex organic compounds composed of carbon, hydrogen, and other elements detected in the geosphere, where the basic structure suggests an unambiguous link with known parent biomolecules (Eglinton and Calvin, 1967; Mackenzie, 1984; Peters and Moldowan, 1993; Hunt et al., 2002; Killops and Killops, 2005; Peters et al., 2005). They can occur in sedimentary rocks and crude oils (Peters and Moldowan, 1993; Peters and Fowler, 2002; Peters et al., 2005). In crude oil, these biomarkers are present in relatively small amounts (usually < 1 % by weight) and usually of lipid origin (Peters and Moldowan, 1993; Killops and Killops, 2005; Peters et al., 2005). These biomarkers can be classified as free or bound biomarkers, where free biomarkers are easily extracted from source rocks and crude oils using common organic solvents or mixtures of solvents (Eglinton et al., 1964; Rubinstein et al., 1979). Bound biomarkers are precursors of the free biomarkers which are chemically bound within the resins and asphaltenes of crude oil or bitumen as well as within the insoluble kerogen matrix of petroleum source rocks, and as such they cannot be extracted by normal extraction procedures. The bound biomarkers are highly resistant to thermal degradation and microbial attack, and are usually liberated from asphaltenes and source rocks via pyrolysis (Gallegos, 1975; Rubinstein et al., 1979; Jones et al., 1987; Love et al., 1995, 1996 & 1997). During burial and maturation the original biological chemical structure only alters minimally (Peters and Moldowan, 1993; Killops and Killops, 2005; Peters et al., 2005). Consequently, biomarkers have many applications in petroleum geochemistry; 1) correlation of oils with each other or suspected source rocks; 2) evaluation of thermal maturity and or/biodegradation; 3) regional variations in the character of oils and source rocks as controlled by organic matter input and characteristics of the depositional environment; and 4) information on kinetics of petroleum generation and basin thermal history (Peters and Moldowan, 1993; Hunt et al., 2002).

For the purpose of this study, the emphasis will be on the Pristane/nC$_{17}$ (Pr/nC$_{17}$) and Phytane/nC$_{18}$ (Ph/nC$_{18}$) isoprenoid/n-alkanes ratios, the C$_{29}$ $\beta\alpha/\alpha\beta$ and C$_{30}$ $\beta\alpha/\alpha\beta$ hopane ratios, and the C$_{31}$ to C$_{32}$ $\alpha\beta$S/($\alpha\beta$S + $\alpha\beta$R) hopane ratios. The extent of thermal maturation is calculated by using the peak areas (or height) of the compound isomers in

the *m/z* 71 and *m/z* 191 mass chromatograms for isoprenoid/n-alkanes and hopane ratios respectively (Peters and Moldowan, 1993; Peters et al., 2005).

2.7.1. Acyclic Isoprenoids.

The common isoprenoid alkanes normally observed in sedimentary rocks and petroleum are pristane (C_{19}) and phytane (C_{20}) (Mackenzie, 1984). Phytol is a major precursor of pristane and phytane in petroleum (Peters and Moldowan, 1993; Peters et al., 2005); where pristane is formed via oxidation and decarboxylation of phytol while phytane is believed to result from dehydration and reduction (Ikan et al., 1975). Pristane/*n*C_{17} and phytane/*n*C_{18} are sometimes used in petroleum correlation studies where both Pr/*n*C_{17} and Ph/*n*C_{18} decreases with thermal maturity of petroleum (Peters and Moldowan, 1993; Peters et al., 2005). The structure of pristane and phytane are shown in Figures 2.4 and 2.5 below, respectively.

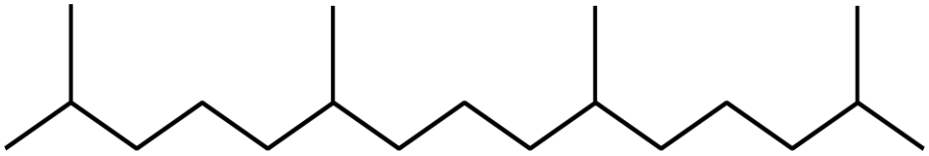


Fig. 2.4. Pristane (2, 6, 10, 14-tetramethylpentadecane) (Peters et al., 2005).

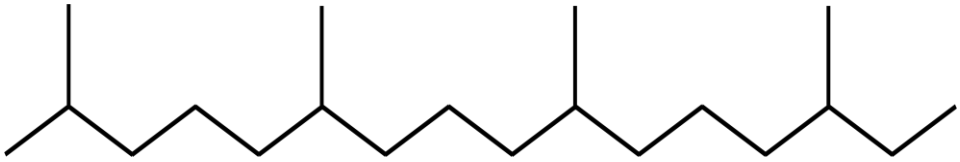


Fig. 2.5. Phytane (2, 6, 10, 14- tetramethylhexadecane) (Peters et al., 2005).

2.7.2. Hopanes.

Hopanes are pentacylic triterpenoids, which are found almost in every geological sample, including petroleum which is sufficiently immature to have allowed preservation (Mackenzie, 1984). The major precursors for the hopanes in source rocks and crude oils include bacteriohopanetetrol and related bacteriohopanes (Peters et al., 2005). The hopanes range from C_{27} to C_{35} but do not include a regular C_{28} member (Mackenzie, 1984), due to the cleavage of the carbon-carbon bond between C-21 and C-22 (resulting in C_{27} hopane) or cleavage of either of the other two carbon-carbon bonds attached to C-22 (resulting in C_{29} hopane) is far more likely than sequential cleavage of two carbon-carbon bonds. The lower hopane pseudohomologs (C_{30} or less) may also be related to C_{30} precursors, such as diploptene or diplopterol (Peters and Moldowan, 1991). Hopanes with more than 30 carbon atoms are commonly called homohopanes, where the prefix homo- refers to additional methylene groups attached to C_{30} hopane (Peters et al., 2005). The hopanes are composed of three stereoisomeric series, namely namely 17α(H), 21β(H) ($\alpha\beta$ hopanes), 17β(H), 21β(H) ($\beta\beta$ hopanes) and 17β(H), 21α(H) ($\beta\alpha$ hopanes) where the compounds in the $\beta\alpha$ series are also called moretanes (Peters and Moldowan, 1993; Peters et al., 2005). The $\beta\beta$ hopane series is thermally unstable, and diagenesis and catagenesis of bacteriohopanetetrol result in a transformation of the 17β(H), 21β(H) precursors to the namely 17α(H), 21β(H) hopanes and 17β(H), 21α(H) moretanes. Similarly, the biological 17β(H), 21β(H)-22R configuration found in bacteriohopanetetrol converts to an equilibrium mixture of 17α(H), 21β(H)-22S and namely 17α(H), 21β(H)-22R ($\alpha\beta$ homophones) (Mackenzie, 1984; Peters and Moldowan, 1991; Peters and Moldowan, 1993). The C_{29} $\beta\alpha/\alpha\beta$ and C_{30} $\beta\alpha/\alpha\beta$ ratios decrease with increasing thermal maturity from about 0.8 in immature bitumen to a value of less than 0.15 in mature source rocks and 0.05 in crude oils (Mackenzie et al., 1980; Seifert and Moldowan, 1980; Peters and Moldowan, 1993). The structure of a C_{30} hopane is shown in Figure 2.6.

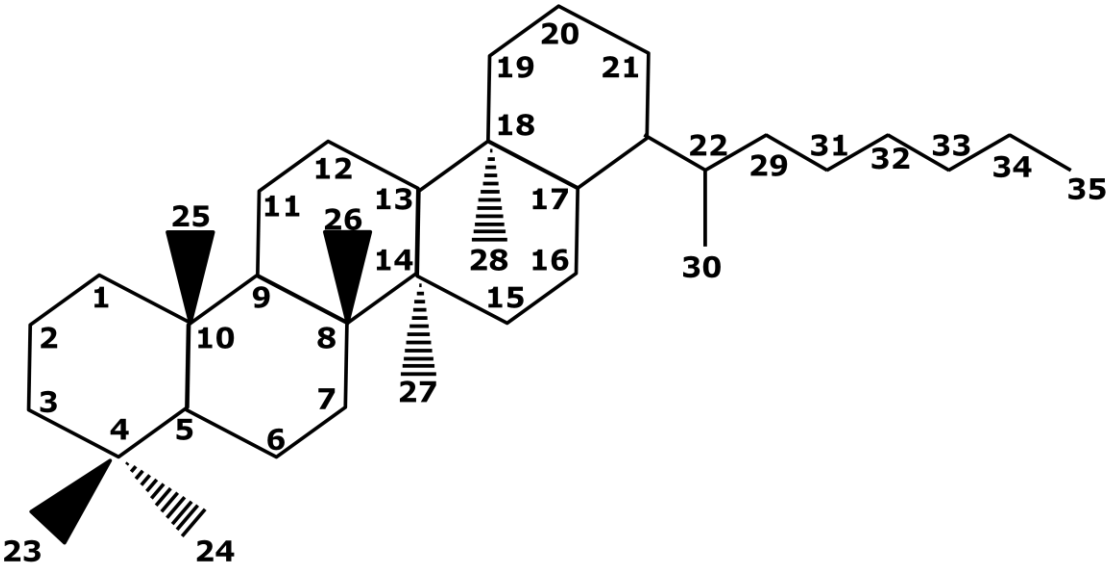


Fig. 2.6. C_{35} Hopane (Peters et al., 2005).

2.7.3. Steranes.

Steranes in petroleums originate from sterols in either lipid membranes of eukaryotic organisms or by enzymes in living things which are unstable during catagenesis and undergoes isomerisation into different sterane geological configurations (Peters and Moldowan, 1993; Peters et al., 2005). Regular steranes ranges from C_{27}-C_{29}, with the biological configuration inherited from its precursor being 5*α*(H), 14*α*(H), 17*α*(H), 20R (*ααα*R steranes), which dominates the sterane distribution of immature sediments. With increasing maturity (increasing burial depth), the *ααα*R steranes isomerises at carbon 14, 17, and 20 to mixtures of 5*α*(H), 14*α*(H), 17*α*(H), 20S (*ααα*S steranes), 5*α*(H), 14*β*(H), 17*β*(H), 20S (*αββ*S steranes), and 5*α*(H), 14*β*(H), 17*β*(H), 20R (*αββ*R steranes) (Mackenzie, 1984). The C_{31} to C_{35} sterane ratios increase from 0 to its equilibrium to 0.60 during maturation (Peters and Moldowan, 1993; Peters et al., 2005). The structure of sterane is shown in Figure 2.7 below.

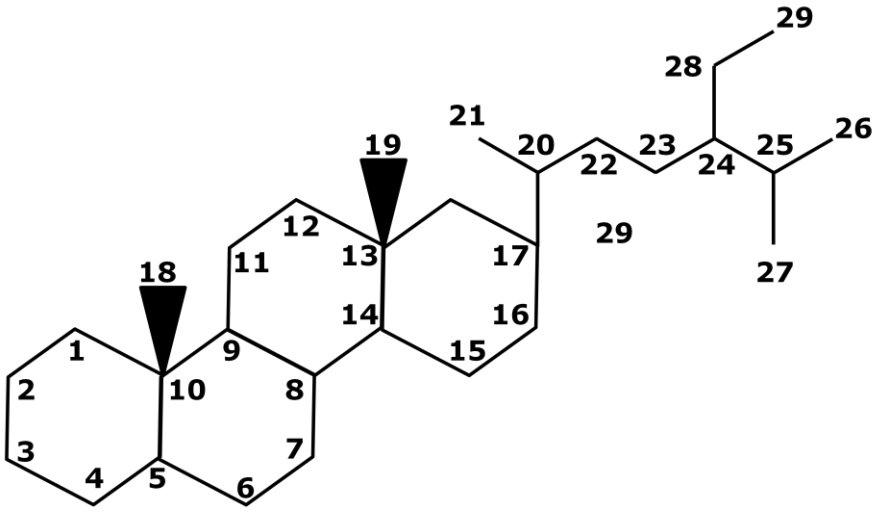


Fig. 2.7. C_{29} Sterane (Peters et al., 2005).

2.8. Pyrolysis.

The prediction of both the quality and quantity of oil and gas generated from a given kerogen remains a key problem in petroleum exploration. In natural systems, it is never possible to quantify directly the amount of gas and light hydrocarbons generated because either the volatile compounds have already been expelled or a loss of gas and light oil occurs during sampling. Hence, pyrolysis techniques can be used in laboratories to simulate and study organic matter evolution occurring in the sedimentary basins and replicating it on a human time scale. Pyrolysis is the decomposition of organic matter through thermal energy (Wampler, 2007). Furthermore, by studying the resulting yields, we are able to understand more on the evolution of organic matter in the sedimentary basins (Domine, 1991; Wampler, 2007).

Many studies have proven that using pyrolysis techniques on coal, kerogens, and petroleum source rocks can generate hydrocarbons and expelled oil similar to the natural trend and yields (Lewan, 1985 & 1997; Blanc and Connan, 1992; Price and Wenger, 1992; Michels et al., 1995b; Behar et al., 2003), simulate organic matter maturation (Monthioux et al., 1985 & 1986; Landais et al., 1990), as well as releasing complete biomarker potential (Peters et al., 1990; Koopmans et al., 1998; Meredith et al., 2004)

There are various types of pyrolysis techniques used such as confined and unconfined pyrolysis, flash pyrolysis and hydropyrolysis, to name a few. In confined pyrolysis, samples are heated in gold tubes or gold cells, where the pressurising medium is usually not in contact with the samples (Landais et al., 1994; Michels et al., 1995a & b; Behar and Hatcher, 1995). For unconfined pyrolysis conditions, the samples are in contact with the pressurising medium which is usually heated in autoclave vessels (Landais et al., 1994; Michels et al., 1995b; Carr et al., 2009; Uguna et al., 2012a, b, & 2013). Experiments using the confined or unconfined techniques can either be heated without water (anhydrous pyrolysis) (Comet et al., 1986; Jones et al., 1987; Koopmans et al., 1998; Behar et al., 2003); with varying amounts of water (hydrous pyrolysis of high water pressure pyrolysis) (Price and Wenger, 1992; Lewan 1997; Landais et al., 1994; Michels et al., 1995b; Carr et al., 2009; Uguna et al., 2012a, b & 2013). Other pyrolysis

techniques such as Rock Eval pyrolysis, hydropyrolysis, micro scale sealed vessel pyrolysis (MSSV) which usually combines flash pyrolysis with gas chromatography or mass spectrometry, where the samples are usually pyrolysed under different heating rates and products are usually quantified by GC or GC-MS throughout the duration of the experiments (van Graas et al., 1981; Tissot and Welte, 1984; van Graas, 1986; Horsfield et al., 1992; Behar and Hatcher, 1995; Love et al., 1995; Fabbri et al., 2002; Behar et al., 2003; Meredith et al., 2004 & 2006; Berwick et al., 2010). For the purpose of this study, we will only focus on anhydrous, low pressure hydrous and high water pressure pyrolysis.

2.8.1. Anhydrous pyrolysis.

Anhydrous pyrolysis is where the samples are heated in the absence of water either in an open or closed system (Behar et al., 1997 & 2003; Carr et al., 2009; Uguna et al., 2012a & b). The Rock Eval pyrolysis is an example of an open anhydrous system where the samples are heated in an inert atmosphere in which a carrier gas is passed over the heated sample. The pyrolysis product is allowed to escape from the sample where it is then swept by the carrier gas and quantified by an FID, or swept through a cold trap to be quantified by GC analysis (Tissot and Welte, 1984; Behar et al., 2003). Another example of an open anhydrous system is hydropyrolysis where samples heated with different heating rates under high hydrogen gas pressure (> 10 MPa) (Meredith et al., 2004; Berwick et al., 2010).

In a closed system, the samples are heated under an inert atmosphere in a sealed reactor such as gold cells or tubes, silica glass tubes, mini-autoclave/tubes or reaction vessels (Comet et al., 1986; Jones et al., 1987; Behar and Hatcher, 1995; Behar et al., 1997; Lewan, 1997; Carr et al., 2009). In this case, the pyrolysate are extracted at the end of the experiment. Anhydrous pyrolysis experiments conducted on kerogens and shales in open and closed systems yields similar mass balances and similar kinetic parameters (Behar et al., 1997). However, Lewan (1997) noted that hydrocarbon gases and liquid hydrocarbon (C_{14+}) generation was higher in an open compared to a closed system. In

contrast, Andresen et al., (1993) reported that open-system pyrolysis generates lower amounts of hydrocarbons as closed-system devices.

Although both open and anhydrous methods have provided information on the potential of kerogen, coals and source rocks to simulate organic matter transformations, their ability to provide low extractable bitumen, and information on generation and expulsion of oil and complete biomarkers from source rocks comparable to a natural system is hindered (Peters et al., 1990; Andresen et al., 1993; Lewan, 1997; Koopmans et al., 1998).

2.8.2. Hydrous pyrolysis.

Hydrous pyrolysis is a hydrothermal experiment which involves the heating of samples in a closed vessel in the presence of water (Lewan, 1985, 1992 & 1997; Lewan et al., 1979). This method of pyrolysis usually requires the heated samples to be in contact and submerged in liquid water, not water vapour or supercritical fluid. When using whole rock samples the presence of water appears to recreate more closely the conditions of naturally occurring environments (Castelli et al., 1990). Hydrous pyrolysis conducted by Lewan (1985), shows that heating organic-rich rocks at 330 °C for 72 h in the presence of liquid water resulted in the generation and expulsion of a petroleum like oil that are absent in olefins, similar to natural crude oils.

Lewan (1985 & 1993) states that the generation of petroleum can be classified into four distinct stages namely, pre-oil generation, incipient oil generation, primary oil generation and post-oil generation. Pre-oil generation represents a thermally immature stage in which the organic matter occurs as a solid insoluble kerogen. During this stage there is lack of expelled oil and no significant change in the amount of kerogen or bitumen. Incipient oil generation begins when thermal stress is sufficient to initiate decomposition of kerogen into a tarry-soluble bitumen enriched in high molecular weight hydrocarbons, and a minor amount of expelled oil. In the primary oil generation stage thermal decomposition of bitumen occurs, resulting in the generation of expelled

oil, which is enriched in saturated hydrocarbons while the amount of kerogen stayed constant or shows only a slight decrease. Thermal decomposition of expelled oil denotes the start of post-oil generation, in which the expelled oil and bitumen thermally decompose into gas and pyrobitumen (Lewan, 1985 & 1993).

Hydrous pyrolysis studies on source rocks has provided information on stages, kinetics and thermal maturation indices of petroleum formation (Lewan, 1985), revealing complete biomarker potential and transformations of a source rock (Peters et al., 1990; Koopmans et al., 1998), maturation of organic carbon isotopes (Lewan, 1983), primary migration and expulsion of oil (Lewan, 1987), oil generation from coals (Kuangzong et al., 1994; Teerman and Hwang, 1991) and increasing carbon dioxide gas and total extractable bitumen and oil, (Andresen et al., 1993, Michels at al., 1995a & b; Lewan, 1997; Carr et al., 2009; Uguna et al., 2012a, b & 2013) compared to anhydrous pyrolysis. These authors all came to a similar conclusion that experiments performed under hydrous conditions may provide a more realistic simulation of organic matter transformations present in the sedimentary basins.

2.8.3. High pressure pyrolysis.

High pressure pyrolysis is when samples are heated using a high pressure medium (> 500 bar) such as inert gas such as helium or argon (Price and Wenger, 1992; Freund et al., 1993; Huang, 1996) or by using liquid such as water or a water and oil mixture (Domine, 1989; Jackson et al., 1995; Michels et al., 1995a & b; Hill et al., 1996; Dalla Torre et al., 1997; Carr et al., 2009; Uguna et al., 2012a, b & 2013). High pressure pyrolysis can also be performed under confined and unconfined conditions. In the case of high pressure confined pyrolysis systems, the heated sample is not in contact with the pressurising medium as the heated sample is sealed in gold bags, gold tubes or Pt-capsules (with or without water), which is then loaded into a high pressure vessel connected an external pressure device (Domine, 1989; Jackson et al., 1995; Michels et al., 1995a & b; Hill et al., 1996; Huang, 1996; Dalla Torre et al., 1997). In high pressure unconfined pyrolysis, the heated sample is placed directly in a high pressure stainless

steel vessel in the absence or presence of water, after which the vessel is sealed under an inert gas atmosphere, and pressure is applied by means of an external pressure device (Landais et al., 1994; Michels et al., 1995a & b; Carr et al., 2009).

2.9. The effects of water on hydrocarbon generation and source rock maturation.

The importance of water in laboratory experiments designed to understand natural processes is well documented in various literatures. Jurg and Eisma, (1964) were the first to suggest that water had a role in natural petroleum generation. They based this conclusion on differences in the products of thermal decomposition of behenic acid in the presence and absence of liquid water with bentonite clay at temperatures from 200 to 275 °C. Their studies show that the ratio of iso-butane and iso-pentane to normal butane and normal pentane, respectively, is much higher without water due to stronger isomerisation compared to experiments with water. Hesp and Rigby, (1973) further confirms this by pyrolyzing the middle fraction of a paraffinic crude oil with and without water at 255 to 375 °C, that water decreases the yield of low molecular weight cracking products and increases the proportion of alkenes among the cracking products. However, recent studies by Pan et al., (2008) shows that under confined pyrolysis of Kukersite kerogen, the ratios of ethene/ethane, propene/propane, isobutane/n-butane, and isopentane/n-pentane, amounts of gaseous hydrocarbons and CO_2 increases with increasing water/OC ratio.

Hydrous pyrolysis have also shown to increase gas generation and pyrolysate yield, lowers reaction rates and organic matter maturation, favouring expulsion of oil, liquid hydrocarbons and biological markers generated from isolated kerogen (Comet et al., 1986; Tannenbaum et al., 1986; Pan et al., 2008), source rocks (Lewan, 1985, 1992 & 1997; Lewan et al., 1979; Michels et al., 1995a) and coals (Teerman and Hwang, 1991; Kuangzong et al., 1994; Behar et al., 2003). These hydrous pyrolysis experiments conducted on the shales, kerogens and coals all generated expelled oil on the surfaces of the samples without olefins being present, similar to those found in natural systems.

However, it was observed that anhydrous and hydrous pyrolysis of asphaltenes generated similar amounts of hydrocarbons amounts and distributions of *n*-alkanes, acyclic isoprenoid alkanes, steranes, and triterpanes (Jones et al., 1987), while in contrast higher amounts of generated hydrocarbon gases, high molecular weight liquid product yields (C_{14+} saturates, aromatics and NSO) was found to be generated during the hydrous pyrolysis of coal and kerogen when compared to anhydrous pyrolysis (Comet et al., 1986; Behar et al., 2003).

Organic matter maturation has also been investigated in both the presence and absence of water. Although there was no significant difference in atomic H/C ratios obtained under both anhydrous and hydrous conditions, vitrinite reflectance values were found to be slightly lower by 0.2 % Ro under anhydrous pyrolysis compared to hydrous pyrolysis of lignite (Behar et al., 2003). The remaining hydrocarbon generation potential as determined by Rock Eval pyrolysis of the residual lignite also showed that the anhydrous residuals had on the average 16 mg more hydrocarbon potential per gram of original lignite than the hydrous residuals, suggesting that there is a better release of the pyrolysis products from the lignite networking the hydrous experiments once generation occurs (Behar et al., 2003). Similarly, Landais et al., (1994) shows that hydrous pyrolysis reduces the Rock Eval Hydrogen Index and T_{max}, and depletes the polars and increases the amount in aromatics and saturates in TSOM (total soluble organic matter).

The generation to biological markers has been studied both in the presence and absence of water. Pyrolysis studies conducted by Koopmans et al., (1998) and Peters et al., (1990) on source rocks shows that hydrous pyrolysis provides the best means of revealing the complete biomarker potential of a rock while under anhydrous conditions, full realization of the biomarker potential, and information is prevented. Comet et al., (1986) also achieved similar results when pyrolysing isolated kerogens under confined conditions in the presence and absence of water at 280 and 330 °C for 72 h where all biomarkers were destroyed under anhydrous pyrolysis, whereas in hydrous pyrolysis experiments the hopanes were present in significant amounts.

The phase of the water present in a reactor during hydrous pyrolysis has also been found to be significant. The presence of liquid water during hydrous pyrolysis was found to enhance the generation and expulsion of oil, as opposed to steam (water vapour) pyrolysis and hydrous pyrolysis which lacked expelled oil phase (Lewan, 1997). Water is considered to have a chemical effect on kerogens during maturation and hydrocarbon generation (Hoering, 1984; Helgeson et al., 1993; Seewald et al., 1998; Siskin and Katritzky, 2001). Michels et al., (1995b) suggested the following mechanisms for the incorporation of water derived hydrogen into hydrocarbons, where the hydrogen exchange between water and an intermediate acidic species through the acid base is either by oxidation reduction mechanism, by transfer of a hydrogen radical from the intermediate compound to the organic radical, or by a radical mechanism. Siskin and Katritzky, (2001) concluded that in the conversion of kerogen into petroleum, water acts as a catalyst, reactant and solvent. In contrast, Stainforth, (2009) concluded that water has insignificant effect on the kerogen reactions due to the fact that the meso and macro-porosity of the condensed kerogens have been removed, where these micropores involved in reactions are of similar size to the petroleum molecules. Although both anhydrous and hydrous pyrolysis methods has provided geochemical information in the understanding of organic matter transformation as described above, the ability of hydrous pyrolysis to closely simulate and enhance organic matter transformation gives it a distinct advantage over anhydrous pyrolysis (Hoering, 1984; Lewan, 1997).

2.10. The effects of pressure on hydrocarbon generation and source rock maturation.

The geochemical models devised to predict source rock maturity and hydrocarbon generation assume that temperature and geological time are the controlling parameters during hydrocarbon generation and source rock maturation, with pressure having no significant effect (Tissot and Welte, 1984). In order to understand the effects of pressure on hydrocarbon generation and source rock maturation, numerous confined and unconfined high pressure pyrolysis studies has been performed.

Most high pressure studies performed using confined pyrolysis systems where the gold bags or capsules acts as the reaction cell under anhydrous and hydrous conditions have so far produced conflicting results. Pressure effects were reported by Monthioux et al., (1985 & 1986) to be insignificant due to similar vitrinite reflectance and Rock Eval T_{max} obtained from confined pyrolysis of lignite and type III humic coals at 250 to 550 °C for 24 h at both low (0.5 kbar) and high (4 kbar) pressure under both anhydrous and hydrous conditions. Huang (1996) also found that that the vitrinite reflectance of lignite samples in sea water pyrolysed in a confined-pressure system over a wide range of temperature and time (250 to 450 °C and up to 305 days) were similar and that water pressures were found to play only minor roles in the development of vitrinite reflectance. Several authors have also have made similar discoveries where the effect of increasing pressure during confined pyrolysis of kerogen have only minor influence on generation kinetics (Freund et al., 1993; Knauss et al., 1997), yields and composition of liquid hydrocarbon (aliphatic and aromatic), bitumen and polar compounds and total soluble extracts (Landais et al., 1994; Michels et al., 1994), gas generation (Michels et al., 1994) and organic matter maturation (Landais et al., 1994) due to similar or identical results obtained at low and high pressure experiments either in the absence or presence of water.

The effects of increased pressure have also been found to be minimal during oil and pure hydrocarbon cracking pyrolysis experiments. Anhydrous pyrolysis experiments using conducted by Horsfield et al., (1992) on oil aliquots from Norwegian North Sea Central

Graben between 300 to 650 °C and on pure hydrocarbons such as *n*-C_{25} (Behar and Vandenbroucke, 1996) between 200 to 425 °C resulted in similar thermal degradation rate, gas and liquid hydrocarbon composition and yields, and pyrobitumen yields were obtained between experiments conducted on low and high pressure.

The effects of increased pressure have also been reported to increase hydrocarbon generation and organic matter maturation. Hill et al., (1994) observed in their confined pyrolysis studies on coals that CO_2 and CH_4 generation, and VR are increased as pressure increases from 90 to 690 bar before decreasing at 2000 bar at temperatures of 300 and 340 °C. Shuai et al., (2006) pyrolysed two immature coals in confined gold reactors from 250 to 600 °C under different pressures (30 and 65 Mpa) showing increasing yield of methane with increasing pressure. Tao et al., (2010) also pyrolysed lignites of different maturities (0.54 % and 0.42 % Ro) in sealed gold tubes at 380 °C, where gaseous hydrocarbon generation from both coals increased as the pressure increases from 50 to 250 MPa.

On the other hand, studies conducted using high pressure pyrolysis techniques via fixed volume autoclave reactors have shown pressure retardation of hydrocarbon generation and source rock maturation. Experiments conducted by Price and Wenger (1992) and Price (1993) using hydrous pyrolysis with kerogen from the Retort Phosphatic Shale shows high pressure retards all aspects of organic matter metamorphism, including hydrocarbon generation, maturation, and thermal destruction. Hatcher et al., (1994) and Wang et al., (2006) performed hydrous pyrolysis experiments on a coal precursors also found that liquid hydrocarbon generation and organic matter maturation was hindered at high pressures in comparison with experiment with lower pressure. Landais et al., (1994) and Michels et al., (1995a) also arrived to the same conclusion when they compared confined and hydrous pyrolsis of kerogen and coals in their studies. Both authors found that the effect of increasing pressure drastically lowers and delays kerogen and coal conversion, retards organic matter maturation and reduces the Rock Eval Hydrogen Index and T_{max}, lowers hydrocarbon generation and total soluble organic matter (TSOM), depletes the polars and increases the amount in aromatics and saturates in

TSOM under hydrous pyrolysis (sample in contact with water) conditions, whereas no pressure effects were observed under confined pyrolysis (using gold cells) conditions at identical experimental conditions. Hydrous pyrolysis experiments conducted on type II Kimmeridge Clay source rocks (Carr et al., 2009; Uguna et al., 2012a) and coals (Uguna et al., 2012b) using autoclaves pyrolysed at temperatures between 310 and 350 °C at water pressures up to 500 bar showed that bitumen and gas generation were retarded under high (500 bar) pressure compared to low pressure (160 bar). However, experiments conducted at 420 °C by Uguna et al., (2012a & b) reveals that neither bitumen plus oil nor gas generation were reduced by when pressure was increased from 300 to 450 bar. This was interpreted as being the effect of high temperature at 420 °C when using insufficient pressure (Uguna et al., 2012b).

The effect of pressure on organic matter maturation has also been investigated using confined and unconfined pyrolysis systems. Sajgo et al., (1986) uses confined pyrolysis to pyrolysed immature alginate and lignite at temperatures ranging from 200 to 450 °C and pressures of 0.06 to 2.5 kbar, where vitrinite reflectances and the formation of hopenes and sterenes and their conversions to hopanes and steranes were retarded in the higher pressure experiments compared to those conducted on low pressures. Dalla Torre et al., (1997) conducted confined pyrolysis in Pt-tubes over a pressure range of 0.5 to 20.0 kbar at temperatures of 200 to 350 °C and run durations of 2, 4, and 7 days where their results show that applied pressure suppresses vitrinite reflectance both in the presence and absence of water, with the retardation effect more significant in the presence of water. Hydrous pyrolysis experiments conducted on type II Kimmeridge Clay source rocks and coals by Uguna et al., (2012a & b) and coals also show that increasing water pressure retards vitrinite reflectances at temperatures of 350 and 420 °C.

The role of pressure during organic matter transformation in geological basins has also been investigated. Geochemical analysis of deeply buried rocks reveals that high fluid pressure may be responsible for the thermal stability of C_{15+} hydrocarbons (Price, 1993). It has also been noted that during organic matter metamorphic reactions, liquid

hydrocarbon generation, vitrinite reflectance, and Rock Eval T_{max} values were all predicted to be retarded at high pressures from geological evidence (Hao et al., 1995 & 1996; Zou and Peng, 2001, Huijun et al., 2004). However, studies conducted by He et al., (2002) on the thermal maturity on overpressure zones suggest that the low vitrinite reflectance and Rock Eval T_{max} from the deeply buried rocks are not caused by the effect of overpressure, but due to contamination of drilling-mud additives and misidentification of the vitrinite macerals.

The role of pressure during oil and pure hydrocarbon cracking has also been investigated. Hill et al., (1996) investigated the thermal cracking of saturate-rich Devonian oil from Canada at 350, 380 and 400 °C and pressures of 90 to 2000 bar. They found different effects of pressure depending on temperature and pressure range. At 350 and 380 °C, a slight decrease was observed for thermal cracking in the 90 to 210 bar range followed by acceleration between 345 and 690 bar and retardation above 690 bar. Al Darouich et al., (2006) performed a set of pyrolysis experiments at 375 °C in gold capsules under high pressures of 400, 800 and 1200 bar for various experiment durations. A substantial decrease of total gas yield is observed when pressure increases from 400 bar to 800 and 1200 bar. The pressure increase also decreases the extent of the global cracking of the light aromatic fraction, the cracking of the unstable charge-classes, and the secondary cracking of the C_{15} to C_{20} and C_{20+} compounds, and the production of insoluble residue is no longer observed. Domine (1989 & 1991) and Domine et al., (1990) also suggested that high pressures considerably hinder the thermal evolution of geological organic matter via their pyrolysis study of *n*-hexane, 2, 4-dimethylpentane and 1-phenylbutane using a gold tubes in the 210 to 15600 bar pressure range at 290 to 365 °C. They found that a**s** pressure is increased, relative light product yields (light alkanes from C_1 to C_5, light alkenes from C_2 to C_5), especially those of alkenes, decrease while those of heavy products (heavy alkanes from C_8 to C_{12}) increase and considerably decreases the overall pyrolysis rate. Enguehard et al., (1989) conducted the pyrolysis of dibutylether in closed reactors in at 200 to 2000 bar and 250 to 300 °C and showed that pressure reduces formation of l-butene via two-fold between 200 and 2000 bar. Jackson et al., (1995) also performed hexadecane pyrolysis experiments in

gold bags for temperatures ranging from 300 to 370 °C and pressures of 150 to 600 bar showing that an increase in pressure retards the rate of reaction of hexadecane cracking by a factor of 2 at 690 bar compared to 150 bar.

Michels et al., (1995a) attributed the retardation effect observed under hydrous pressure conditions to the nature of the pressuring medium (pyrolyzed sample in contact with pressurised water) rather than the pressure itself which leads to the conflicting between the previous studies regarding the role of pressure. According to Uguna et al., (2012b), under high pressure confined pyrolysis conditions the pressure applied is not in direct contact with the pyrolysed sample but applied externally on the wall of the gold bag/capsule and products (gaseous and liquid) generated give rise to a volume increase and this causes the gold bag/capsule to expand due to the high flexibility of gold. Uguna et al., (2012b) also suggested that the minimal pressure effect observed in confined pyrolysis might be due to the product pressure acting against the applied external pressure rather than transmitting it, with the wall of the gold cell/tube aiding as a barrier. In high water pressure pyrolysis experiments the water pressure applied is in direct contact with the pyrolysed sample and the system is completely filled with rock and water, such that the products that are generated either find it difficult to escape from the rock (liquid products) or have little or no space to occupy (gaseous products), resulting in an observed pressure retardation effect (Uguna et al., 2012b).

2.11. The effects of minerals on hydrocarbon generation and source rock maturation.

The influence of mineral on organic matter during thermal maturation has long been studied. Several studies conducted during confined pyrolysis of fatty acids (Jurg and Eisma, 1964; Shimoyama and Johns, 1972), isolated kerogens (Horsfield and Douglas, 1980; Espitalié et al., 1984; Tannenbaum and Kaplan, 1985; Tannenbaum et al., 1986; Pan et al., 2008), oil (Pan et al., 2010) and coals (Horsfield and Douglas, 1980; Saxby et al., 1992; Koopmans et al., 1998) all come to the conclusion that catalysis occurs under anhydrous conditions, but no significant effect is evident under hydrous conditions. Under anhydrous confined conditions, the presence of various clay minerals (especially montmorillonite) produces higher proportions of light fractions (C_1 to nC_{10}) and aromatic compositions, higher ratios of isobutane/*n*-butane and isopentane/*n*-pentane and higher amounts of coke are formed compared to experiments conducted without the presence of these clay minerals. However, in these studies the pyrolysis experiments were performed in sealed glass tubes with low pressures and very large reaction volumes relative to the amounts of reactants. Authors such as Pan et al., (2008), Carr et al., (2009) and Uguna et al., (2012a & b) have stated in their studies that the reaction medium of these pyrolysis experiments is different from that of natural source rocks.

Tests closer to natural conditions were performed by Espitalié et al., (1984) in a closed confined system in the presence of water and at moderate temperature (360 °C for 48 h). Mixtures were made up of 50 mg of the reference oil shale (7.4 % organic carbon), 200 mg of illite and 200 µ1 of distilled water. The amounts of bitumen extracted by chloroform obtained after heating were 25 % lower in the case of illite than in the reference oil shale alone (heated in the same conditions), with a depletion of the NSO compounds (34.5 % compared to 46.2 % for the reference oil shale). Eglinton et al., (1986) performed experiments on a kerogen (Type II) isolated from the Kimmeridge Blackstone band that has been artificially matured under hydrous pyrolysis conditions in the presence of three clay minerals (montmorillonite, illite, kaolinite), calcium carbonate and limonite in order to investigate the influence of the latter on the organic products. Pyrolysis experiments were performed in the presence of water and a 20-fold

excess of mineral phase at two different temperatures (280 and 330 °C) for 72 h. They revealed that all samples generated much greater amounts of organic-soluble products with calcium carbonate producing a large yield (40 % wt/wt). In addition, a higher sterane and triterpane isomerisation level for the pyrolysate of the same kerogen in the presence of calcium carbonate as compared to pure kerogen and kerogen with the different clay minerals. Pan et al., (2008) conducted confined pyrolysis (gold capsules) experiments on isolated Kukersite kerogens and oil in the presence and absence of water and various minerals (kaolinite, montmorillonite, calcite, and dolomite) at a fixed pressure of 50 MPa and temperatures between 240 to 400 °C. The author reports that the ratios of isobutane/*n*-butane and isopentane/*n*-pentane generally increase with temperature and mineral acidity, ratios of ethene/ethane and propene/propane generally decrease with temperature and mineral acidity.

Other than minerals, transition-metals are also advocated as critical mechanism in determining the extent, composition, and timing of natural gas generation (Mango et al., 1994; Mango, 1996). Mango et al., (1994) and Mango (1996) carried out reactions in U tubes in with pure transition metal compounds in the absence and presence of source rocks. Both studies show that the presence of transition metals promotes the formation of *n*-alkanes compounds, natural gas and increases reaction rates. Larsen and Hu, (2006) also demonstrated that the amounts of CH_4 and CO_2 produced in hydrous pyrolysis of kerogen are higher in the presence of pyrite than in the absence of pyrite, and they further increased with the addition of iron bearing mineral mixtures (FeS, FeS_2, and Fe3O4), implying that iron-bearing minerals can enhance the hydrous pyrolysis reaction of a kerogen. In contrast, hydrous pyrolysis experiments conducted by Lewan et al., (2008) on type II kerogen at 330 and 355°C for 72 h shows that the presence of transition metals did not increase gas generation due to the catalytic poisoning by the bitumen during early stages of thermal maturation.

Overall, these studies show that such interactions between kerogen, bitumen, oil, minerals and possibly water could also occur during petroleum formation in a sedimentary basin. Recent studies by Pan et al., (2012) show that under confined

systems (gold capsules) that oil cracking was enhanced in the presence of oil compared to coal pyrolysed alone. The existence of these multiple phases (especially in the presence of water) might cause difficulty to understand what is happening in hydrous pyrolysis, understanding the chemistry that is occurring, and extrapolating from model compound studies to kerogen reactions. Despite requiring intimate association with reactants to be effective, it is the exception rather than the norm for oil to be in direct contact with mineral surfaces in rocks due to most reservoirs (and probably all source rocks) remain water-wet during the petroleum generating phase (Pepper and Dodd, 1995). The expelled organics especially oil maybe floating on the water, unable to react with either the minerals or the kerogen, whereas reactions between the kerogen and the minerals can occur only when they come into contact at their interface (Larsen and Hu, 2006). However, water is ubiquitous in geological basins and the interaction with these reactant phases (source rock/kerogen, bitumen, mineral matter) cannot be excluded.

Chapter 3: Experimental techniques and methodology.

3.1. Experimental techniques.

3.1.1. Gas chromatography.

Gas chromatography is use to separate volatile mixtures in nanogram quantities during passage over the surface of an immobile material, where the vapourised sample in a gas stream goes through a column containing a stationary liquid (gas-liquid chromatography or GLC) or a solid phase (gas-solid chromatography or GSC). The components migrate at different rates due to the differences in boiling point, solubility or adsorption. The mobile phase for both GLC and GSC is gas. Gas chromatography has a widespread of uses, almost entirely for organic materials. The technique is rapid, simple and can cope with very complex mixtures (100 or more components) and very small samples (nanogram quantities), and is useful for both qualitative and quantitative analysis. A gas chromatograph instrument consists of an injection port, a regulated gas cylinder supplying the carrier gas, a column enclosed in a thermostatically controlled oven, a detector and a recorder. The injection port is located ahead of the column and is designed to allow the sample to be introduced into the carrier gas-stream in as narrow a band as possible. The samples injected must be volatile and thermally stable at operating temperatures of usually from ambient to over 400 °C, programmed to suit the elution process. The samples are injected through a self-sealing silicone rubber septum usually located at the top of the column (coil of stainless steel, glass or fused silica tubing) using a 1-10 µl capacity syringe for gases, and 1-50 µl for liquids. The carrier gases (mobile phase) generally used are nitrogen, argon, helium and hydrogen, depending on the type of column (packed or capillary), cost and the detector being used. Helium and hydrogen are the preferred gases for capillary columns because chromatographic efficiency diminishes more slowly with increasing flow rate above the optimum with these gases than with nitrogen, thus facilitating faster separations. There are two types of columns that are commonly used, namely the packed column usually made of metal (stainless steel, copper, and aluminium) or glass, and the capillary column usually made of quartz or flexible silicone. These columns are generally 1 to 100 m in length with an internal

diameter between 0.1 mm and about 3 mm). A continuous flow of gas elutes the components from the column in order of increasing distribution ratio (i.e. the ratio of the concentration of the solute in the stationary phase to that in the mobile phase) from where they pass through a detector (which monitors the carrier gas as it emerges from the column and responds to changes in its composition as solutes are eluted) connected to a recording system. The response of the detector is recorded as a chromatogram plot (a plot of the detector response against time) whereby each separate component detected registers a peak on the chromatogram. Gas chromatography has very widespread use, almost entirely for organic materials. The technique is rapid, simple and can cope with very complex mixtures (100 or more components) and very small samples (nanograms), it is useful for both qualitative and quantitative analysis (Fifield and Kealey, 2000; Killops and Killops, 2005). A schematic diagram of a gas chromatograph is shown in Figure 3.1 (Fifield and Kealey, 2000).

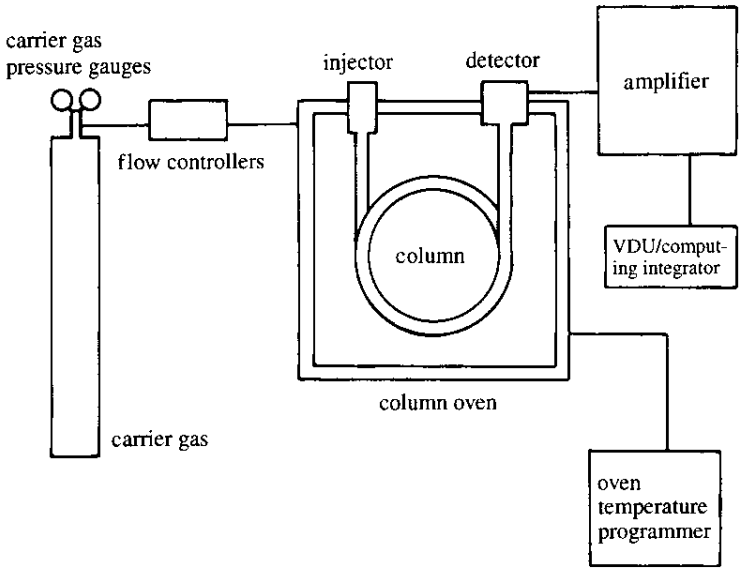


Fig. 3.1. Schematic diagram of a gas chromatograph (Fifield and Kealey, 2000).

3.1.2. Gas chromatography-mass spectrometry.

Gas chromatography-mass spectrometry (GC-MS) is the combination of a gas chromatograph and a mass spectrometer with the aid of an interface (a device for transporting the effluent from the gas chromatograph to the mass spectrometer) linking both instruments. The gas chromatograph separates the components of a mixture in time, and the mass spectrometer provides information that aids in the structural identification of each component. Identification of separated components in GC-MS is achieved by feeding the effluent gases from the GC column directly to the mass spectrometer. The carrier gas (usually helium), is pumped away with the aid of a jet-orifice separator (usually for packed columns) while allowing the sample vapours to pass on into the mass spectrometer. The gas chromatograph separates the components of a mixture and the mass spectrometer characterizes each of the components individually. Eluted components can be detected either by monitoring the total ion current (TIC) in the mass spectrometer or by selected ion monitoring (SIM). TIC is the sum of the currents generated by all the fragment ions of a particular compound, and is proportional to the instantaneous concentration of that compound in the ionising chamber of the mass spectrometer. SIM involves monitoring the ion current for a selected mass fragment (*m/z*) value characteristic of a particular compound or a group of compounds. Detection by SIM can be very selective and often specific. SIM is particularly useful in trace analysis because it is more sensitive than TIC. The technique of GC-MS is now well established as one of the most powerful analytical tools available for the study of complex samples (Fulton et al., 1996; Fifield and Kealey, 2000; Killops and Killops, 2005). A schematic diagram of a gas chromatograph-mass spectrometer is shown in Figure 3.2 below (Fifield and Kealey, 2000).

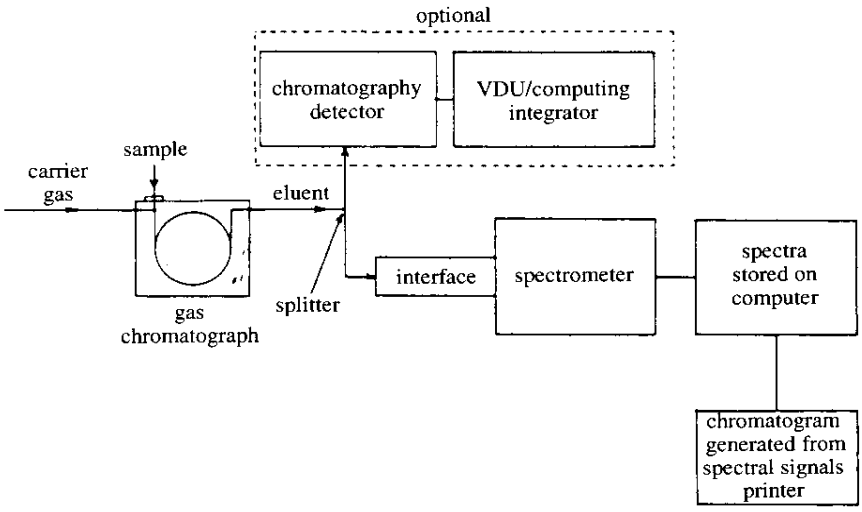


Fig. 3.2. Schematic diagram of a gas chromatograph-mass spectrometer (Fifield and Kealey, 2000).

3.2. Methodology.

3.2.1. Sample description.

The samples used in this study are organic rich immature type-II Kimmeridge Clay Formation (KCF) source rocks from the coastal outcrop at Kimmeridge bay in Dorset, United Kingdom. The pyrolysis experiments were conducted on source rocks of different total organic carbon (TOC) contents (14, 25 and 30 %). The 14 and 25 % TOC source rocks was crushed to particle sizes of between 180-425 μm, while the 30 % KCF source rocks was crushed to between 2-5 mm in size. The purpose for conducting experiments with varying TOC contents is to study the effect of hydrocarbon generation based on different TOC content of the source rocks. Table 3.1 lists the Rock Eval and vitrinite reflectances (VR) of the immature samples used in this study.

TOC (%)	Sample size	S_1 (mg/g TOC)	S_2 (mg/g TOC)	HI (mg/g TOC)	Mean VR (% Ro)
14	180-425 μm	2	89	616	0.3
25	180-425 μm	3	175	684	0.4
30	2-5 mm	5	194	639	0.4

Table 3.1. Geochemical data for Kimmeridge Clay Samples.

3.2.2. Pyrolysis equipment and experimental procedures.

The pyrolysis equipments and experimental procedures used in this study is the same used and described previously in Carr et al., (2009) and Uguna et al., (2012a & b). Pyrolysis experiments were performed on the KCF source rocks at temperatures of 320-420 °C (temperature accuracy ±1 °C) and run time 7-48 h under low pressure hydrous (115-310 bar) and high water pressure (450-900 bar) conditions. The pyrolysis equipments comprises a Parr 4740 series Hastalloy (22 ml cylindrical) pressure vessel (rated to 648 bar at 350 °C), connected to a pressure gauge rated to 690 bar (Fig. 3.3a), or a Hastalloy pressure vessel (25 ml cylindrical) pressure vessel (rated to 1400 bar at

420 °C) designed by Strata Technology, Sunbury-on-Thames, UK, connected to an Autoclave Engineers pressure gauge and rupture disc rated to 950 bar (Fig. 3.3c). The total internal volume of the assembled empty Parr and Strata pressure vessels (including volume of pipe work and pressure gauge) was estimated to be 34 ml and 31 ml, respectively. Heat was applied by means of a fluidised sand bath (connected to a compressed air source) controlled by a temperature gauge. Temperature was also monitored independently by means of a K-type thermocouple attached to the outside of the vessel and recorded by computer every 10 s.

The KCF samples was charged into a pressure vessel together with the required amount of water for low pressure hydrous and high-water pressure hydrous conditions, or without water for anhydrous pyrolysis conditions. The water added into the vessel was aerated with nitrogen for 30 min in order to reduce the amount of air/oxygen present. The pressure vessel is then assembled, after which the reactor is repeatedly flushed with nitrogen to evacuate the air in the reactors head space and finally pressurised with 2 bar of nitrogen to keep the atmosphere in pressure vessel relatively inert throughout the experiment. Low pressure hydrous experiments were conducted using the Parr pressure vessel at 320, 340 and 350 °C by the addition of 10 or 15 ml distilled H_2O to the vessel, giving pressures of 115 bar (at 320 °C), 160 bar (at 340 °C) and 180 bar (at 350 °C). The same pressure vessel was also used for experiments at 420 °C where the low pressure (310 bar) experiments were conducted using 10 ml H_2O and the high pressure (450 bar) experiments were performed using 15 ml H_2O. The amount of water used for the experiments was varied to control the pressure at all temperatures, except for the high pressure (500 and 900 bar) runs at 350 and 420 °C, where the added water was insufficient to generate the required pressure and additional water was pumped into the vessel to increase the pressure.

The high pressure (500 and 900 bar) experiments at 350 and 420 °C were performed using the Strata pressure vessel in a similar fashion to the other experiments described earlier, with the vessel initially filled with 20 ml H_2O. The sand bath (connected to a compressed air source) was preheated to the required temperature and left to equilibrate

(approx. 30 min), after which the pressure vessel was lowered onto the sand bath with a constant air flow through the sand bath. After lowering the pressure vessel onto the sand bath, the vessel was connected to the high-pressure line and allowed to attain its maximum vapour pressure (approx. 20 min) before adding more water to increase the pressure. This is to ensure that excess water was not added to the vessel that could result in excessive pressure, thereby creating a safety issue. To apply a high liquid water pressure to the system, a compressed air driven liquid pump was used where the emergency pressure release valve B was first closed (Figs. 3.3b and d), and valve A opened until a pressure slightly higher than the vapour pressure of the experiment was displayed on the external pressure gauge (to avoid losing any content of the vessel when the reactor valve C was opened). A high liquid water pressure was then applied to the system by first opening valve C and immediately gradually opening valve A to add more distilled water to the pressure vessel. To attain high pressures of 500 and 900 bar (350 and 420 °C for 24 h), the vessel was initially pressurised to about 440 and 880 bar respectively, where the final pressure was reached by thermal expansion of the additional water and generated gas. When the required pressure (either 500 or 900 bar) was attained, valve C was closed to isolate the reactor from the high-pressure line, and valve A was also closed to prevent more water going to the pressure line. Then valve B was opened to vent the excess pressure in the line. The experiment was then allowed to run (leaving valve C tightly closed to avoid losing generated products) for the required time, after which the sand bath was switched off and left to cool to ambient temperature before product recovery.

Fig. 3.3a. Complete set up of Parr pressure vessel.

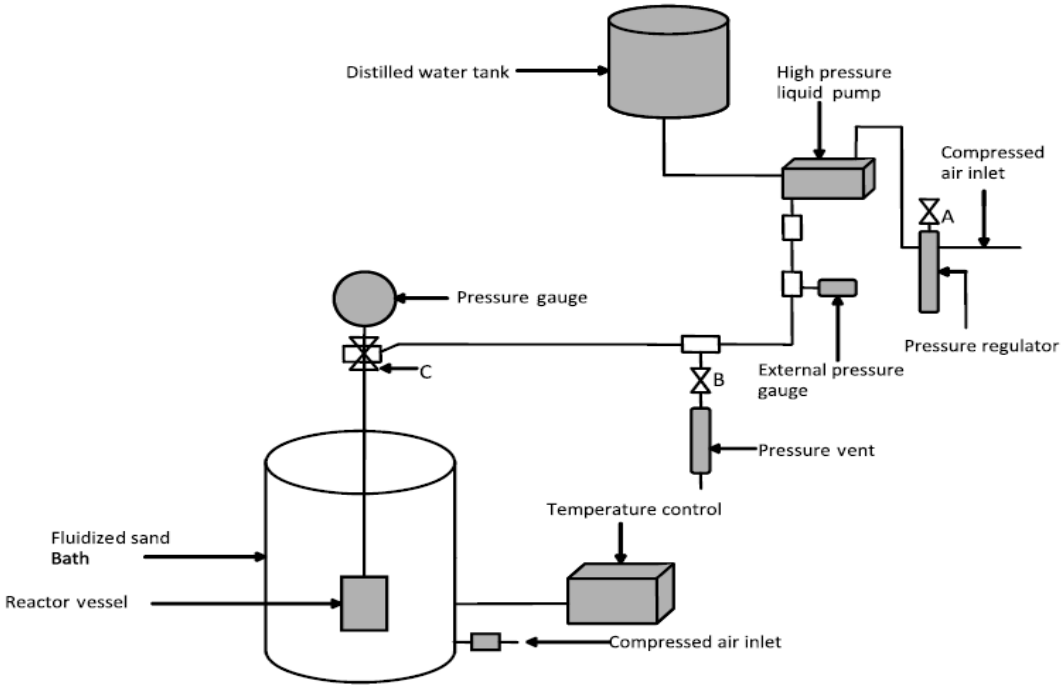


Fig. 3.3b. Schematic diagram of the Parr pyrolysis equipment.

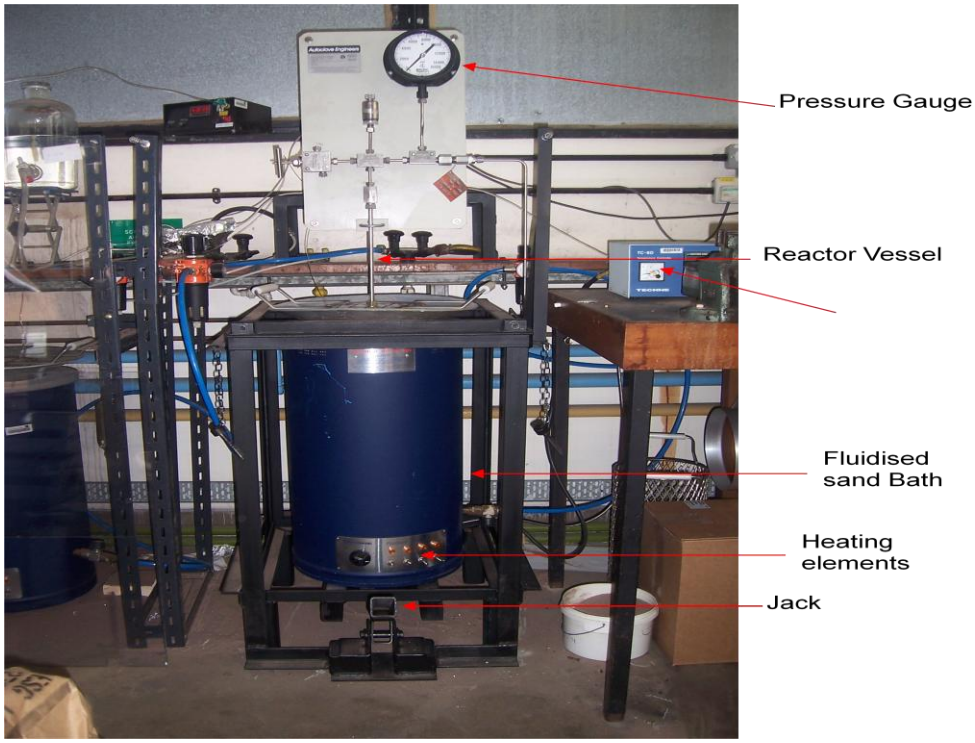


Fig. 3.3c. Complete set up of Strata pressure vessel.

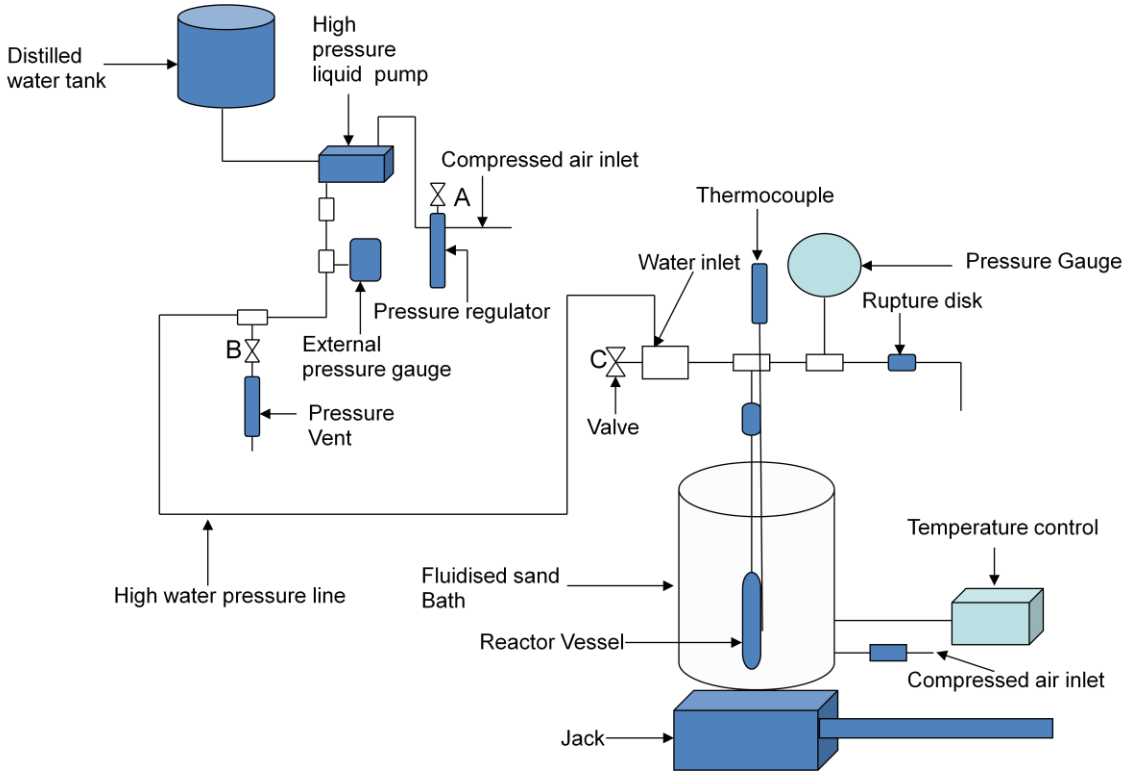


Fig. 3.3d. Schematic diagram of the Strata pyrolysis equipment.

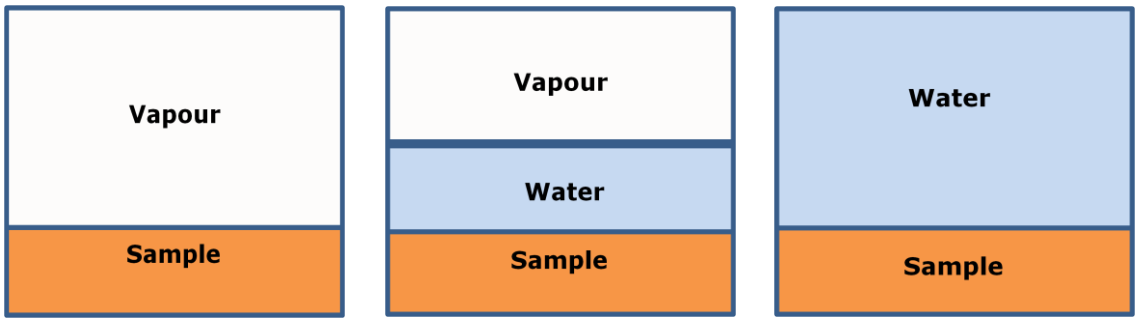
3.2.3. Pyrolysis configurations and experiments.

There are 3 types of pyrolysis configurations that were used in this study namely;

A) Anhydrous pyrolysis - The pressure vessel initially contains the sample and inert vapour (Fig. 3.4a)

B) Hydrous pyrolysis - The pressure vessel initially contains the sample, liquid water and a reduced vapour space (Fig. 3.4b)

C) High water pressure pyrolysis - the pressure vessel is completely filled with liquid water and sample, leaving no vapour space (Fig. 3.4c).



A) B) C)

Fig. 3.4. Types of pyrolysis configurations used.

Overall, the pyrolysis experiments were performed in 5 different ways as described below:

3.2.3.1. Bitumen generation.

A unique characteristic of using Kimmeridge Clay Formation (KCF) source rock is that it has the advantage of reaching a clear plateau in terms of maximum bitumen generation before the onset of bitumen cracking to oil as demonstrated from the series of hydrous pyrolysis experiments conducted by Carr et al., (2009) and Uguna et al., (2012a) on the 25 % TOC KCF source rocks. The results from Carr et al., (2009) shows that hydrous

pyrolysis experiments at 320 °C for 24 h with 10 ml (115 bar) and 15 ml (125 bar) H_2O generates 1004 and 955 mg/g TOC of bitumen, respectively. The same hydrous pyrolysis experiments conducted by Uguna et al., (2012a) at 350 °C for 6 h with 10 ml (180 bar) and 15 ml (210 bar) H_2O generates 998 and 997 mg/g TOC of bitumen, respectively; whereas at 350 °C for 12 h with 10 ml (180 bar) and 15 ml (210 bar) H_2O generated slightly lower amounts with 851 and 818 mg/g TOC of bitumen, respectively. The results presented by these authors indicate that a very clear demarcation can be achieved between the maximum bitumen generation (at 320 °C for 24 h or at 350 °C for 6 h) before the onset of subsequent cracking of the bitumen (at 350 °C for 12 h) from the 25 % TOC KCF source rocks.

In order to find maximum bitumen generation from the 14 % TOC KCF source rocks, a series of hydrous pyrolysis experiments or 'bitumen generation' experiments were performed under hydrous conditions at 320 °C with 10 ml and 15 ml H_2O for 24 and 48 h, at 340 °C with 10 ml and 15 ml H_2O for 7 and 14 h, and at 350 °C with 15 ml H_2O for 14 h. A temperature of 340 °C for a time of 7 h with 15 ml H_2O were the conditions selected for bitumen generation from the 14 % TOC KCF source rocks due to the short run time to achieve the maximum bitumen yield (discussed in Section 4.2). The experimental condition selected for the 25 % TOC KCF source rocks to generate maximum bitumen yields is at 350 °C for 6 h with 10 ml H_2O, and for the 30 % TOC KCF source rocks is at 350 °C for 6 h with 15 ml H_2O (Carr et al., 2009; Uguna et al., 2012a & b).

At the end of the bitumen generation experiment, the equipment was switched off and allowed to cool to ambient temperature followed by analysis of the generated C_1-C_4 hydrocarbons gases (Section 3.3). The generated bitumen was then isolated from residual rock or 'partially matured source rock' by Soxhlet extraction with DCM/methanol (93:7 vol: vol) mixture for 48 h, and the amounts of bitumen and partially matured source rock was determined (Section 3.4) and analysed (Section 3.6, 3.7 and 3.8). This was to enable the partially matured source rock and bitumen to be pyrolysed at higher temperatures in isolation (Section 3.2.3.2 and 3.2.3.3, respectively)

or in mixtures (Section 3.2.3.4) as described below. A flow chart of the bitumen generation experiment and analytical operations is shown in Figure 3.5.

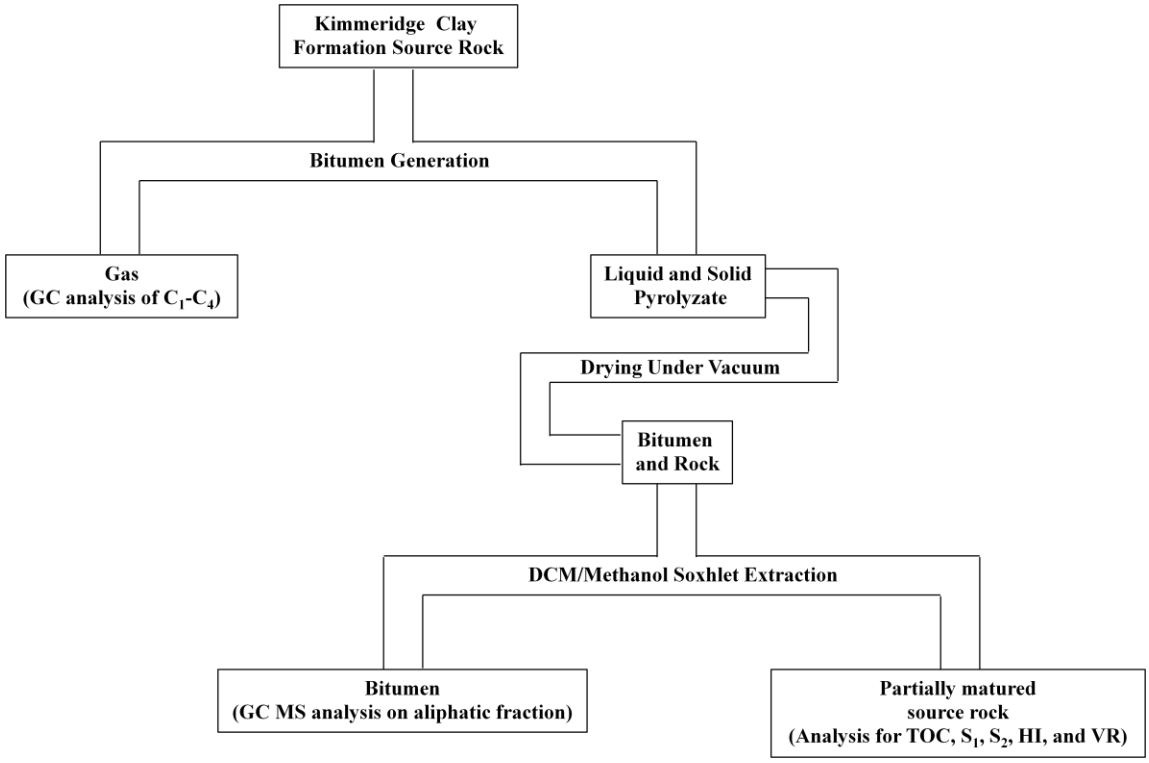


Fig. 3.5. Flow chart of experimental and analytical operations for the bitumen generation experiments.

3.2.3.2. Pyrolysis of partially matured source rock in isolation.

The amount of partially matured residual rock recovered from bitumen generation experiments (Section 3.2.3.1 previously) were pyrolysed further at 350 and 420 °C for 24 h under low pressure hydrous (180-310 bar) and high water pressure (450-900 bar) conditions. The amount of partially matured residual rock sample used is approx. 5.8, 2.5, or 1.9 g, which is generated from the bitumen generation experiments using the 14, 25 or 30 % TOC KCF source rocks, respectively. The purpose of this study was to investigate if the absence of bitumen had any effect on VR obtained from the partially matured source rock by comparing these results with the whole rock experiments (Section 3.2.3.5) in which the bitumen was not separated from the source rock. A flow

chart of the isolated partially matured source rock pyrolysis experiment and analytical operations is shown in Figure 3.6.

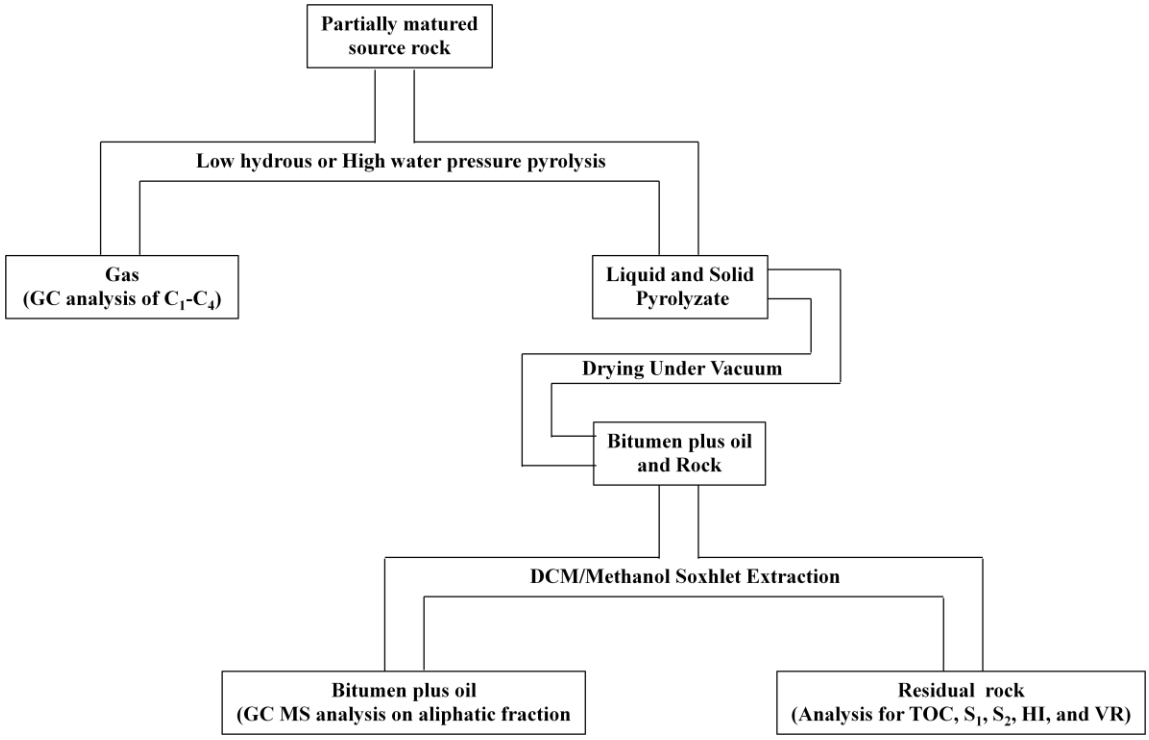


Fig. 3.6. Flow chart of experimental and analytical operations for the isolated partially matured source rock experiments.

3.2.3.3. Pyrolysis of bitumen in isolation.

The amount of bitumen recovered from bitumen generation experiments (Section 3.2.3.1 previously) were also subjected to further pyrolysis at 350 and 420 °C for 24 h under low pressure hydrous (180-310 bar) and high water pressure (450-900 bar) conditions. The amount of bitumen sample used is approx. 0.8, 0.9, or 0.9 g, which are generated from the bitumen generation experiments using the 14, 25 or 30 % TOC KCF source rocks, respectively. Another set of experiments were conducted where the bitumen generated from the 14 % TOC source rocks was pyrolysed at 420 °C for 24 h in the presence of powdered montomorillonite clay minerals under anhydrous (25 bar) and high water pressure (450 bar) conditions, where the amount of montmorillonite/bitumen

used was in a 5:1 (wt:wt) ratio, similar to the mineral composition described by Scotchman (1987 & 1990) and Morgans-Bell et al., (2001). To conduct pyrolysis experiments in the presence of the montmorillonite, the bitumen generated from the 14 % TOC source rocks (0.8 g) was first adsorbed on to approx. 3.9 g of montmorillonite using dichloromethane and is left to evaporate before the experiment. The purpose of this study was to investigate the combined effects of mineral matter, kerogen/bitumen interactions and water pressure on gas yields. A flow chart of the isolated bitumen pyrolysis experiment and analytical operations is shown in Figure 3.7.

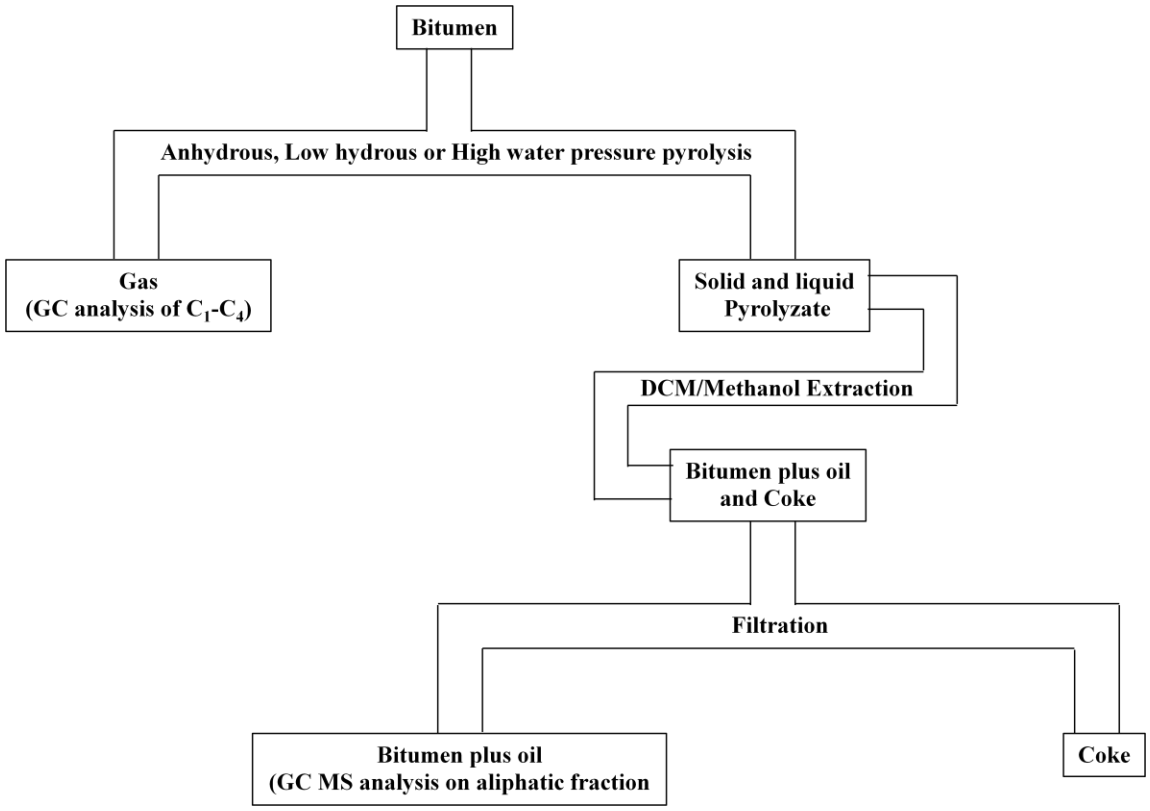


Fig. 3.7. Flow chart of experimental and analytical operations for the isolated bitumen experiments.

3.2.3.4. Pyrolysis of mixtures of partially matured source rock and bitumen (Recombined Mixture).

Pyrolysis experiments were performed on the recombined partially matured source rock and generated extracted bitumen mixtures generated from the 14 and 30 % TOC source rocks. To conduct a recombined mixture experiment, the recovered bitumen (approx. 0.8 or 0.9 g generated from bitumen generation experiments using the 14 and 30 % TOC source rocks, respectively) was adsorbed to the partially matured source rock (approx. 5.8 or 1.9 g generated from bitumen generation experiments using the 14 and 30 % TOC source rocks, respectively) in the pressure vessel using dichloromethane and left to evaporate before the experiment. Similar to the previous experiments described earlier (Section 3.2.3.2 and 3.2.3.3), pyrolysis experiments were conducted at 350 and 420 °C for 24 h under low pressure hydrous (180-310 bar) and high water pressure (450-500 bar). When the bitumen is adsorbed back to the source rock the contact will probably be mainly at the surface of the rock, and this mixture will not have the intimate or direct contact with mineral matter and kerogen as was the case with whole rock experiments (Section 3.2.3.5 below) when the bitumen was not extracted. The experiments were performed in order to investigate if bitumen or heavy oil that is adsorbed to the surface of source rock can interact with mineral matter during hydrocarbon generation reactions, by comparing this experiment to those of whole rock (Section 3.2.3.5 below). A flow chart of the mixture of partially matured source rock and bitumen (recombined mixture) pyrolysis experiment and analytical operations is shown in Figure 3.8.

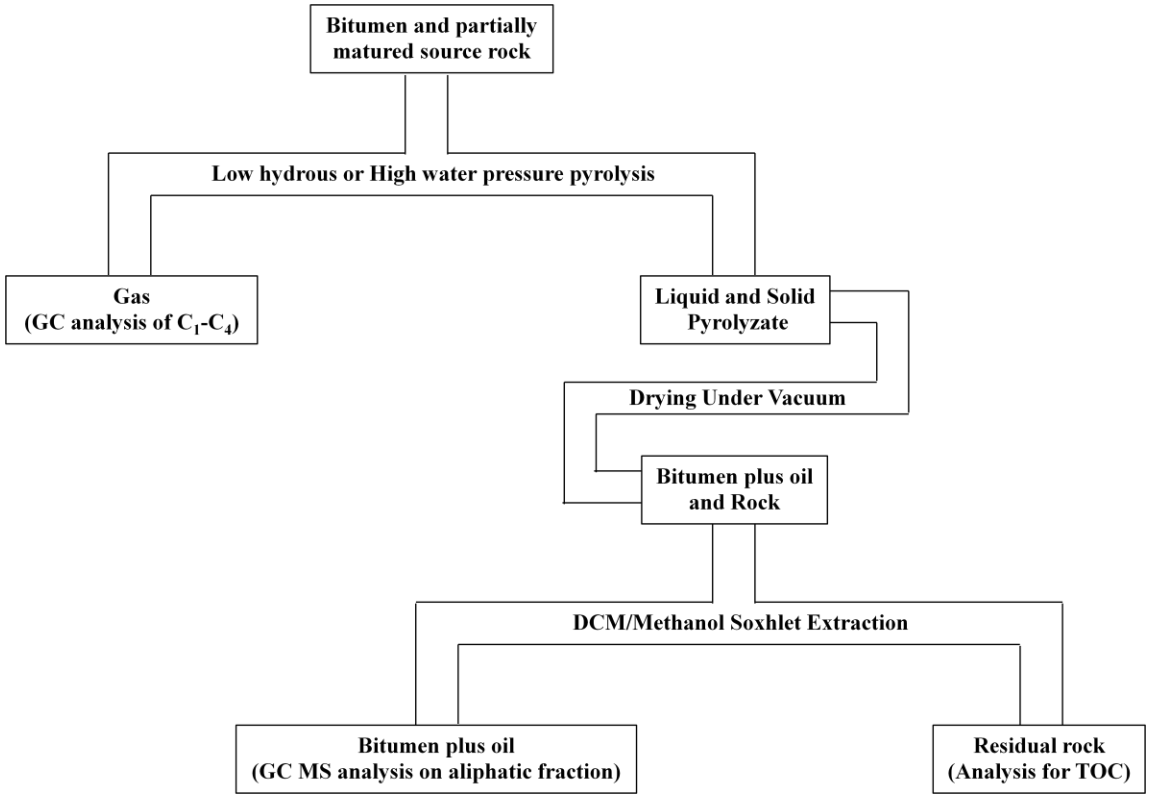


Fig. 3.8. Flow chart of experimental and analytical operations for the recombined mixture experiments.

3.2.3.5. Whole rock pyrolysis.

In this study, the initial rock was pyrolysed at 350 and 420 °C for 24 h under low pressure hydrous (180-310 bar) and high water pressure (450-900 bar). The experiments were performed on 1 g TOC whole rock, which is approx. 6.9, 4.0 and 3.3 g by weight from the 14, 25 and 30 % TOC whole rocks, respectively. This study on whole rock was conducted to investigate the effect of water pressure on hydrocarbon gas generation and source rock maturation, as well as to allow comparison with partially matured source rock and bitumen when pyrolysed individually (isolated fractions) or in recombined mixtures (Section 3.2.3.4) in order to ascertain the influence of mineral matter and reactant phase (source rock, minerals and bitumen) on hydrocarbon gas generation and

source rock maturation. A flow chart of the whole rock pyrolysis experiment and analytical operations is shown in Figure 3.9.

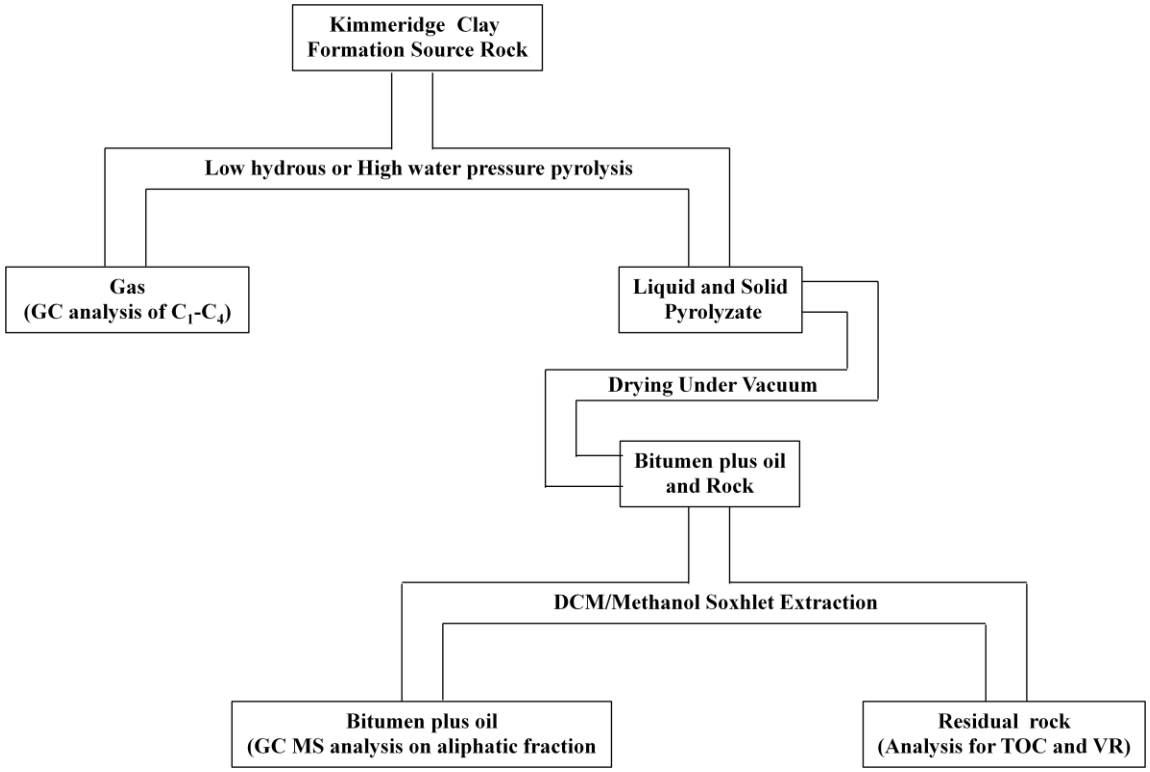


Fig. 3.9. Flow chart of experimental and analytical operations for the whole rock experiments.

3.3. Gas analysis.

The total volume of the hydrocarbon gases (C_1-C_4) generated was collected and measured from the pressure vessel using a gas tight syringe and transferred into a gas bag. The gases are immediately analysed on a Carlo Erba HRGC 5300 gas chromatograph (GC) fitted with a flame ionization detector (FID) operating at 200 °C. 10 µl of the gas samples were injected at 100 °C and separation performed on a Varian Poraplot-Q fused silica 25 m x 0.32 mm x 10 µm column, with helium as the carrier gas. The oven temperature was programmed for 70 °C (2 min hold) to 90 °C (3 min hold) at 40 °C min^{-1}, then to 140 °C (3 min hold) at 40 °C min^{-1}, and finally to 180 °C (49 min hold) at 40 °C min^{-1}. Individual gas yields were determined quantitatively in relation to methane as an external gas standard, and the total yields of the hydrocarbon gases generated calculated using the total volume of generated gas collected in relation to the aliquot volume of gas introduced to the GC.

3.4. Recovery of bitumen plus oil, partially matured source rock and coke.

After gas collection and analysis, the reactor was dismantled and the water was decanted from the pyrolysed rock with the aid of a pasture pipette. In the case of hydrous or high water pressure pyrolysis experiments involving the use of source rock samples (whole rock in Section 3.2.3.1 and 3.2.3.5, partially matured source rock in Section 3.2.3.2, or recombined mixtures in Section 3.2.3.4), the reactor containing the wet residual rocks are slowly dried at 45 °C for 4 h in a vacuum oven. After drying, the dried source rocks were transferred into a pre-extracted cellulose thimble and Soxhlet extracted for 48 h using 200 ml of dichloromethane/methanol mixture (93:7 vol:vol) at 45 °C. To ensure maximum recovery of the products (bitumen plus oil and residual rocks), the inside pipe fitting of the pressure gauge were thoroughly rinsed with the DCM until clear and were also added into the pre-extracted cellulose thimble prior to Soxhlet extraction. However, for experiments using the 30 % TOC source rock samples (2-5 mm particle size); the source rock samples are Soxhlet extracted for a period of 1 week with the DCM/methanol mixture to ensure that all of the bitumen plus oil inside the rock chips is

recovered. After extraction, the mixture is gently rotary-evaporated until almost dry and the remaining mixture is transferred into a pre-weighed glass vial with DCM using a pasture pipette. The contents in the glass vial are left to air dry for 48 h after which the weight of the bitumen plus oil and the residual source rocks can be determined.

In the case of bitumen cracking experiments (Section 3.2.3.3), water was separated from the liquid product (bitumen plus oil) using the same method described previously. The product (bitumen plus oil) generated from a 350 °C bitumen cracking experiment is transferred directly into a round bottom flask by washing the reactor with dichloromethane (DCM) with the aid of a pasture pipette, after which the liquid product is Soxhlet extracted for 24 h at 45 °C. After Soxhlet extraction, the mixture is gently rotary-evaporated until almost dry and the remaining mixture is transferred into a pre-weighed glass vial with DCM using a pasture pipette. The contents in the glass vial are left to air dry for 48 h after which the weight of the bitumen plus oil can be determined. For experiments conducted at 420 °C, where coke is present, or when montmorillonite clay minerals are used during the isolated bitumen cracking experiments, these solid residues were also added together with the liquid for Soxhlet extraction. After Soxhlet extraction, the mixture of liquid and solid products undergoes vacuum filtration through a pre-weighed filter paper in order to determine the amount of solid residues (coke/montmorillonite). After filtration, the filtrate undergoes rotary evaporation similar to the procedures describe previously in order to determine the amount of bitumen plus oil and solid products (coke and/or montmorillonite).

The liquid products generated from the bitumen generation experiments will be termed as ‘bitumen’ whereas for experiments at 350 and 420 °C for 24 h the liquid product will be termed as ‘bitumen plus oil’. The expelled oil fraction was not treated separately from the bitumen due to the difficulty of separating the oil that is adsorbed on the rock particles without simultaneously dissolving the bitumen in the extracting solvent (dichloromethane). In addition, 1 g TOC of starting material from the Kimmeridge source rocks used in this study were not sufficient to generate a significant amount of expelled oil, as only a small amount was observed at the end of the run.

3.5. Fractionation method.

The bitumen plus oil yield samples and expelled oil samples are separated into aliphatic and aromatic fractions by pre-extracted silica/alumina adsorption column chromatography. The aliphatic hydrocarbons were eluted in 15 ml *n*-hexane. The aromatic fractions were subsequently recovered in 15 ml *n*-hexane/dichloromethane (3:2 vol:vol). The yields of each fraction were determined after evaporation over a period of 2 days in pre-weighed vials.

3.6. GC-MS analysis of aliphatics.

Gas chromatography-mass spectrometry (GC-MS) analyses of the aliphatic fractions (1 µl in DCM) were performed on a Varian Instruments CP 3800 gas chromatograph interfaced to a 1200 Quadrupole mass spectrometer (ionising energy 70 ev, source temperature 280 °C). Separation was performed on a fused silica capillary column (50 m x 0.32 mm i.d) coated with BPX5 phase (0.25 µm thickness). Helium was employed as the carrier gas with a temperature program of 50 °C (2 min) to 350 °C (28 min) at 5 °C min^{-1}. Eluted components were monitored by selected ion monitoring where the selected ions monitored included *m/z* 71 (n-alkanes) and *m/z* 191 hopanes.

3.7. Total organic carbon analysis.

The TOC was determined by combusting samples in an oxygen-rich atmosphere in a Thermo Electron FlashEX 1112 Elemental analyser, controlled by EAGER300 software for Windows (Thermo Electron, Milan, Italy). The instrument consisted of quartz reactor tube, containing sequential beds of copper oxide as the oxidising reactant, and copper wire as the reductant, located in a furnace held at 900 °C. A continuous stream of helium was passed through the reactor at 140 ml min^{-1}. The introduction of the sample (ca 4 mg) into the reactor was co-incident to the injection of an aliquot of pure oxygen, which ensured the flash combustion of organic matter in sample. The products of this combustion were CO_2, H_2O, SO_X, and NO_X, which were then removed from the

oxidation stage of the reactor by the stream of helium. Reactions in the reduction bed of the reactor yielded a final mixture of CO_2, H_2O, N_2, and SO_2, which were then passed into a GC column (stainless steel packed column, 2 m x 0.5 mm, Porapak Q) for separation. Individual components were then quantified by TCD, by comparison to the same combustion products of a known amount of standard material (BBOT; 2,5-bis (5'-tert-butyl-2-benzoxazolyl) thiopene.

3.8. Vitrinite reflectance measurements.

The vitrinite reflectance measurements were done by Dr Andrew Carr from Advanced Geochemical Systems Ltd and conducted here at the University of Nottingham. Vitrinite reflectance measurements were obtained from immature whole rock and the Soxhlet extracted residual rock mounted in epoxy resins. Prior to reflectance measurements, samples were grounded and polished using successively finer grades on silicon carbide and colloidal silica to produce a scratch free polish. Measurements were made on a Leitz Orthoplan microscope fitted with an MPV control and photometer head. Using the Leitz MPV computer program the samples were examined in white light using oil immersion objectives, while reflectance was measured using a green filter with a peak transmission of 547 nm as required (use BS or ISO standard number). The results were expressed as arithmetic means of measurements taken in oil immersion (% R_o).

Chapter 4: Results for whole rock, isolated partially matured rock and bitumen and recombined mixtures experiment.

The results presented in this chapter is on pyrolysis experiments conducted with the 14 and 25 % TOC source rocks, whereas the results obtained from the 30 % TOC source rocks is discussed in Chapter 5. The results from all pyrolysis experiments presented in Chapter 4 and 5 are normalised to 1 g of starting TOC of the initial source rock, except when indicated otherwise.

4.1. Whole rock experiments.

4.1.1. Gas yields.

The individual and total C_1-C_4 gas yield (mg/g TOC of starting rock), gas dryness ratio (C_1/(C_1-C_4)), and alkene/alkane gas ratios generated from the whole rock experiments at 350 and 420 °C for 24 h are listed in Tables 4.1a and b from the 14 and 25 % TOC source rocks, respectively. Table 4.1c lists the mean of the duplicate results in Tables 4.1a and b, while Table 4.1d shows the relative standard deviations (%) between the duplicate experiments (1 and 2) in Tables 4.1a and b. The relative standard deviation for the alkane gases (methane, ethane, propane and butane) and total gas yields (C_1-C_4) from the duplicate experiments presented in Table 4.1d, as well as the duplicate experiments presented throughout this chapter and in chapter 5 are $\leq$ 2 %, showing that the experiments are reproducible.

At 350 °C for 24 h (Table 4.1c), the total gas yield from the 14 % TOC source rocks were highest at 180 bar (21 mg/g TOC) and reduced at 500 bar (17 mg/g TOC). The 25 % TOC source rocks also follows the same trend at 350 °C for 24 h where the total gas yields at 180, 500 and 900 bar were 39, 21 and 15 mg/g TOC, respectively. The reducing gas yield is due to increasing water pressure retarding bitumen cracking to gas, which is consistent with the previous studies (Carr et al., 2009; Uguna et al., 2012a & b).

When the temperature was increased to 420 °C for 24 h, a significant increase in gas yield was observed for both low (310 bar) and high pressure (450 bar) experiments (Table 4.1c) compared to experiments conducted at 350 °C. This increase in gas yield is due to the severe cracking of the initial bitumen and resultant oil generated at higher temperature. As pressure increases from 310 to 450 bar at 420 °C for 24 h for the 14 % TOC source rocks, there is no significant difference in gas yield generated at 310 bar (188 mg/g TOC) and 450 bar (191 mg/g TOC). The 25 % TOC source rocks at 420 °C for 24 h follows the same trend at 500 bar (181 mg/g TOC) and 900 bar (189 mg/g TOC) where no significant difference in gas yields were generated, apart from 310 bar (223 mg/g TOC), where the gas yield was higher. The higher gas yield from the 25 % TOC source rocks generated at 310 bar is due to direct cracking of the generated bitumen to gas under super heated steam conditions (310 bar) compared to supercritical water conditions at 500 and 900 bar, where less gas was generated due to enhanced oil generation and expulsion from bitumen cracking (discussed in Section 4.1.2). Overall, the leveled gas yields observed at 420 °C for 24 h at 310 and 450 bar from the 14 % TOC source rocks, and at 500 and 900 bar from the 25 % TOC source rocks was interpreted by Uguna et al., (2012a & b) that the applied water pressure was insufficient to retard gas generation due to water promotional effects being more dominant over the effects of water pressure compared to 350 °C. The gas yields generated from the 25 % TOC source rocks are slightly higher under all experimental conditions. The higher gas yields is due to the 25 % TOC source rocks having a higher initial S_2 (175 mg/g TOC) and slightly higher HI (684 mg/g TOC) compared to the 14 % TOC source rocks, where the S_2 and HI values are 89 and 616 mg/g TOC, respectively (Table 3.1 shown previously).

In conjunction to the decreasing gas yields, the alkene/alkane ratios for both source rocks at 350 °C for 24 h also decreases with increasing water pressure (Table 4.1c). When pressure was increased from 180 to 500 bar, the 14 % TOC source rocks shows a decrease in ethene/ethane and propene/propane ratio by a magnitude of 8 and 5, respectively. The 25 % TOC source rocks follows the same trend going from 180 to 500 bar, where the ethene/ethane and propene/propane ratio is reduced by a magnitude of 2

and 1.5, respectively. At 900 bar and 350 °C for 24 h, the ethene/ethane ratio from the 25 % TOC source rocks remains unchanged compared to 500 bar and 350 °C, whereas the propene/propane ratio is decreased by a magnitude of 1.4 compared to 500 bar and 350 °C. The decrease in gas yields observed with increase in pressure is consistent with previous studies where water pressure has been found to retard gas generation (Carr et al., 2009; Uguna et al., 2012a & b).

The gas dryness ratios at 350 and 420 °C shows that the hydrocarbon gases was slightly higher for the high pressure experiments as opposed to their corresponding low pressure experiments, indicating more methane were generated in relation to the other hydrocarbon gases from the high pressure experiments. Overall, the dryness ratio from all of the whole rock pyrolysis experiments can be considered as similar under all experimental conditions for both source rocks, ranging from 0.31 to 0.37.

Table 4.1a. Individual and total gas (mg/g TOC of starting rock), gas dryness ratio ($C_1/(C_1\text{-}C_4)$), and alkene/alkane (C_2H_4/C_2H_6; C_3H_6/C_3H_8) ratio from duplicate experiments (1 and 2) for the whole rock experiments at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	$\frac{C_2H_4}{C_2H_6}$	$\frac{C_3H_6}{C_3H_8}$
Low pressure 1	180	350	6.73	0.09	6.45	0.45	5.20	1.93	21	0.32	0.014	0.087
Low pressure 2	180	350	6.66	0.10	6.36	0.39	5.06	1.97	21	0.32	0.016	0.077
High pressure 1	500	350	5.90	0.01	5.14	0.06	4.05	1.70	17	0.35	0.002	0.015
High pressure 2	500	350	6.04	0.01	5.20	0.08	4.11	1.71	17	0.35	0.002	0.019
Low pressure 1	310	420	68.2	0.06	53.4	0.39	49.2	17.1	188	0.36	0.001	0.008
Low pressure 2	310	420	68.1	0.06	53.5	0.36	49.3	16.7	188	0.36	0.001	0.007
High pressure 1	450	420	73.0	0.03	52.4	0.27	49.0	16.7	191	0.38	0.001	0.006
High pressure 2	450	420	73.5	0.04	52.5	0.34	47.8	16.9	191	0.38	0.001	0.007

[1 & 2] duplicate runs

Table 4.1b. Individual and total gas (mg/g TOC of starting rock), gas dryness ratio ($C_1/(C_1\text{-}C_4)$), and alkene/alkane (C_2H_4/C_2H_6; C_3H_6/C_3H_8) ratio from duplicate experiments (1 and 2) for the whole rock experiments at 350 and 420 °C for 24 h (25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	$\frac{C_2H_4}{C_2H_6}$	$\frac{C_3H_6}{C_3H_8}$
Low pressure 1	180	350	11.7	0.10	11.7	0.65	9.52	5.36	39	0.30	0.009	0.068
Low pressure 2	180	350	11.8	0.10	11.8	0.59	9.42	5.33	39	0.30	0.008	0.063
High pressure	500	350	6.95	0.03	6.15	0.21	4.99	2.75	21	0.33	0.005	0.042
High pressure	900	350	5.00	0.02	4.35	0.10	3.45	1.85	15	0.34	0.005	0.029
Low pressure 1	310	420	78.4	0.08	65.3	0.64	56.5	22.3	223	0.35	0.001	0.011
Low pressure 2	310	420	78.6	0.07	65.4	0.72	56.4	22.2	223	0.35	0.001	0.013
High pressure	500	420	63.3	0.14	47.6	0.83	44.9	24.5	181	0.35	0.003	0.018
High pressure	900	420	69.6	0.10	49.5	0.60	45.1	23.6	189	0.37	0.002	0.013

[1 & 2] duplicate runs

Table 4.1c. Mean values from duplicate experiments (1 and 2) for the whole rock experiments at 350 and 420 °C for 24 h in Table 4.1a and b (14 and 25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	$\frac{C_2H_4}{C_2H_6}$	$\frac{C_3H_6}{C_3H_8}$
Low pressure												
14 % TOC set	180	350	6.70	0.10	6.41	0.42	5.13	1.95	21	0.32	0.016	0.082
25 % TOC set	180	350	11.8	0.10	11.8	0.62	9.47	5.35	39	0.30	0.008	0.065
High pressure												
14 % TOC set	500	350	5.97	0.01	5.17	0.07	4.08	1.71	17	0.35	0.002	0.017
25 % TOC set	500	350	6.95	0.03	6.15	0.21	4.99	2.75	21	0.33	0.005	0.042
25 % TOC set	900	350	5.00	0.02	4.35	0.10	3.45	1.85	15	0.34	0.005	0.029
Low pressure												
14 % TOC set	310	420	68.2	0.06	53.5	0.38	49.3	16.9	188	0.36	0.001	0.008
25 % TOC set	310	420	78.5	0.08	65.4	0.68	56.5	22.3	223	0.35	0.001	0.012
High pressure												
14 % TOC set	450	420	73.3	0.04	52.5	0.31	48.4	16.8	191	0.38	0.001	0.006
25 % TOC set	500	420	63.3	0.14	47.6	0.83	44.9	24.5	181	0.35	0.003	0.018
25 % TOC set	900	420	69.6	0.10	49.5	0.60	45.1	23.6	189	0.37	0.002	0.013

Table 4.1d. Relative standard deviation (%) between the duplicate experiments (1 and 2) in Table 4.1a and b.

Experiment	Pressure (bar)	Temp (°C)	Relative standard deviation (%)				
			CH_4	C_2H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)
Low pressure							
14 % TOC set	180	350	1	1	2	1	0
25 % TOC set	180	350	1	1	1	0	0
High pressure							
14 % TOC set	500	350	2	1	1	0	0
Low pressure							
14 % TOC set	310	420	0	0	0	2	0
25 % TOC set	310	420	0	0	0	0	0
High pressure							
14 % TOC set	450/500	420	0	0	2	1	0

4.1.2. Bitumen plus oil and liquid hydrocarbon yields, and maturity assessment of aliphatic fractions of bitumen plus oil.

The bitumen plus oil, aliphatic, aromatic, and total liquid hydrocarbon (aliphatic plus aromatic) yields (mg/g TOC of starting rock) generated from the whole rock experiments at 350 and 420 °C for 24 h are listed in Tables 4.2a and b, for the 14 and 25 % TOC source rocks, respectively. Table 4.2c lists the mean of duplicate results in Table 4.2a and b.

At 350 °C for 24 h (Table 4.2c), the bitumen plus oil yield for the whole rock experiments were lowest at 180 bar (563 mg/g TOC) and increased at 500 bar (609 mg/g TOC) from the 14 % TOC source rocks. The 25 % TOC source rocks follows the same trend at 350 °C for 24 h where the total bitumen plus oil yield generated at 180, 500 and 900 bar is 576, 643 and 666 mg/g TOC, respectively. The overall increase in bitumen plus oil yield with increasing water pressure at 350 °C is due to the effect of pressure preserving the bitumen and resultant oil from cracking into gas, which is consistent with the decreasing gas yield at 500 and 900 bar compared to 180 bar as shown previously in Table 4.1c. This result is also consistent with previous studies by Carr et al., (2009) and Uguna et al., (2012a & b). When the temperature was increased to 420 °C, the severe cracking of the bitumen to oil and gas at this temperature leads to a reduction in overall bitumen plus oil yields, which is consistent with the higher gas yields generated at 420 °C in comparison to 350 °C (Table 4.1c, previously). The bitumen plus oil yield from the 14 % TOC source rocks shows an increase with increasing water pressure at 420 °C, where the bitumen plus oil yield increases from 101 mg/g TOC at 310 bar to 159 mg/g TOC at 450 bar. Similarly, the bitumen plus oil yield from the 25 % TOC source rocks increases from 151 mg/g TOC at 310 bar, to 322 at 500 bar, and to 328 mg/g TOC at 900 bar (Table 4.2c), which is consistent with the gas yields described previously in Section 4.1.1. The increase in bitumen plus oil yield with the increase in water pressure at 420 °C is due to more bitumen plus oil obtained under supercritical water conditions (500 and 900 bar) and the promotional effect of water, compared to super heated steam conditions (310 bar) where the experiment lacked expelled oil due to the bitumen

cracking directly to gas. Lower bitumen plus oil yields were generated from the 14 % TOC source rocks under all experimental conditions due to the lower S_2 and slightly lower HI of the starting rock compared to the 25 % TOC source rocks as mentioned previously in Section 4.1.1 and shown in Table 3.1.

At 350 °C, the amount of aliphatic and aromatics for both source rocks are slightly reduced when pressure was increased from 180 to 500 bar, where the total liquid hydrocarbon yields were reduced by 10 % and 20 % from the 14 and 25 % TOC source rocks, respectively. At 900 bar, the total liquid hydrocarbon yields from the 25 % TOC source rocks were reduced further by 8 % compared to 500 bar. This is consistent with the previous studies where liquid hydrocarbon formation was retarded under liquid water pressure (Price and Wenger, 1992; Michels et al., 1995a & b). However, when pressure was increased from 310 to 450 bar at 420 °C, the aromatic yields and total liquid hydrocarbon yields also increases with pressure, whereas the aliphatic yields remains similar for both source rocks. At 420 °C, the total liquid hydrocarbon yields from the 14 % TOC whole rock experiments increases by 41 % going from 310 to 450 bar. The 25 % TOC whole rock experiments at 420 °C also shows an increase of 41 %, going from 310 to 500 bar, and an additional 12 % increase from 500 to 900 bar. The liquid hydrocarbons (aliphatic and aromatic) generated from the 14 % TOC source rocks were higher compared to the 25 % TOC source rocks at 350 °C. This might be due to the two source rocks having different liquid hydrocarbon generating potential. However, at 420 °C, higher liquid hydrocarbon yields were generated from the 25 % TOC source rocks due to more bitumen plus oil remaining compared to the 14 % TOC source rocks.

Table 4.2a. Bitumen plus oil, aliphatic, aromatic, and total liquid hydrocarbon (aliphatic plus aromatic) yields (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the whole rock experiments at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Bitumen plus oil	Liquid hydrocarbons		
				Aliphatic	Aromatic	Ali + Aro
Low pressure 1	180	350	564	79	108	187
Low pressure 2	180	350	561	78	106	184
High pressure 1	500	350	611	68	100	168
High pressure 2	500	350	607	65	103	168
Low pressure 1	310	420	103	10	43	53
Low pressure 2	310	420	98	10	50	60
High pressure 1	450	420	161	9	69	78
High pressure 2	450	420	157	9	71	80

[1 & 2] duplicate runs

Table 4.2b. Bitumen plus oil, aliphatic, aromatic, and total liquid hydrocarbon (aliphatic plus aromatic) yields (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the whole rock experiments at 350 and 420 °C for 24 h (25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Bitumen plus oil	Liquid hydrocarbons		
				Aliphatic	Aromatic	Ali + Aro
Low pressure 1	180	350	579	33	71	104
Low pressure 2	180	350	572	33	75	108
High pressure	500	350	643	30	55	85
High pressure	900	350	666	29	49	78
Low pressure 1	310	420	152	5	55	60
Low pressure 2	310	420	150	7	62	69
High pressure	500	420	322	5	87	92
High pressure	900	420	338	6	97	103

[1 & 2] duplicate runs

Table 4.2c. Mean values from duplicate experiments (1 and 2) for the whole rock experiments at 350 and 420 °C for 24 h in Table 4.2a and b (14 and 25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Bitumen plus oil	Liquid hydrocarbons		
				Aliphatic	Aromatic	Ali + Aro
Low pressure						
14 % TOC set	180	350	563	79	107	186
25 % TOC set	180	350	576	33	73	106
High pressure						
14 % TOC set	500	350	609	67	102	168
25 % TOC set	500	350	643	30	55	85
25 % TOC set	900	350	666	29	49	78
Low pressure						
14 % TOC set	310	420	101	10	47	56
25 % TOC set	310	420	151	6	59	65
High pressure						
14 % TOC set	450	420	159	9	70	79
25 % TOC set	500	420	322	5	87	92
25 % TOC set	900	420	338	6	97	103

The maturity of the bitumen plus oil samples were assessed using the biomarker ratios; Pr/nC_{17} and Ph/nC_{18} ratios, the C_{29} and C_{30} $\beta\alpha/\alpha\beta$ hopane ratios and the C_{31} and C_{32} $\alpha\beta$S/($\alpha\beta$S + $\alpha\beta$R) hopane ratios (Peters and Moldowan, 1993; Peters et al., 2005). Table 4.3 lists the biomarker ratios from the 14 % TOC whole rock experiments at 350 °C for 24 h.

The Pr/nC_{17} ratio at 180 bar (1.92) and 500 bar (1.93) at 350 °C for 24 h were similar, whereas the Ph/nC_{18} ratio indicates a more mature bitumen plus oil were generated at 180 bar (1.68) due to the lower ratio compared to 500 bar (1.77). The lower C_{29} (0.25) and C_{30} (0.33) $\beta\alpha/\alpha\beta$ hopane ratios at 180 bar compared to those at 500 bar (0.33 and 0.37 for the C_{29} and C_{30} $\beta\alpha/\alpha\beta$ ratios, respectively) also indicated a mature bitumen plus oil at 180 bar. However, the C_{31} and C_{32} $\alpha\beta$S/($\alpha\beta$S + $\alpha\beta$R) hopane ratios shows similar maturities were achieved for the bitumen plus oil yields at 180 (0.54 and 0.54, for the C_{31} and C_{32} $\alpha\beta$S/($\alpha\beta$S + $\alpha\beta$R) ratios, respectively) and 500 bar (0.53 and 0.51, for the C_{31} and C_{32} $\alpha\beta$S/($\alpha\beta$S + $\alpha\beta$R) ratios, respectively). Overall, the Ph/nC_{18} biomarker indicates that faster thermal cracking are occurring at low pressure (180 bar), whereas slower thermal cracking was observed when pressure was increased to 500 bar. This is consistent with the higher gas yields generated from 180 bar compared to 500 bar as previously mentioned. The C_{29} and C_{30} $\beta\alpha/\alpha\beta$ hopane ratios indicates that under 180 bar, better isomerisation reactions are occurring compared to 500 bar.

Table 4.3. Biomarker ratios [Pr/nC_{17} and Ph/nC_{18} ratios, C_{29} and C_{30} $\beta\alpha/\alpha\beta$ hopane ratios, and C_{31} to C_{32} $\alpha\beta$S/($\alpha\beta$S + $\alpha\beta$R) hopane ratios] for the 14 % TOC whole rock experiments at 350 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Isoprenoids		Hopanes			
					C_{29}	C_{30}	C_{31}	C_{32}
			Pr/nC_{17}	Ph/nC_{18}	$\beta\alpha/\alpha\beta$	$\beta\alpha/\alpha\beta$	S/(S+R)	S/(S+R)
Low pressure								
14 % TOC set	180	350	1.92	1.68	0.25	0.33	0.54	0.54
High pressure								
14 % TOC set	500	350	1.93	1.77	0.33	0.37	0.53	0.51

4.1.3. Residual TOC, vitrinite reflectance (VR) and carbon mass balances.

The residual rock mass (g), residual rock TOC (%) and vitrinite reflectance (% Ro) for the whole rock experiments at 350 and 420 °C for 24 h are listed in Tables 4.4a and b, from the 14 and 25 % TOC source rocks, respectively. Table 4.4c lists the mean of duplicate results in Table 4.4a and b.

At 350 °C for 24 h (Table 4.4c), the residual TOC at 180 bar (5.0 % TOC) and 500 bar (5.1 % TOC) were similar from the 14 % TOC source rocks. However, the 25 % TOC source rocks shows a reduction from 180 bar (14.8 % TOC) to 500 bar (11.8 % TOC), which is also the same as 900 bar (11.6 % TOC). This is due to high pressure (500 and 900 bar) pressure retarding bitumen cracking which resulted in less pyrobitumen being formed at high pressure and is consistent with the higher bitumen plus oil yield generated from high pressure experiments (500 and 900 bar) compared to the low pressure (180 bar) experiments at 350 °C. At 420 °C for 24 h (Table 4.4c), the residual TOC from the 14 % TOC source rocks at 310 bar (8.9 % TOC) were higher compared to 450 bar (7.7 % TOC), respectively. Similarly, the 25 % TOC source rocks follows the same trend where residual TOC obtained at 310, 500 and 900 bar were 14.4, 11.1 and 11.0 % TOC, respectively. The reduction in residual TOC with increasing water pressure at 420 °C is also consistent with the higher bitumen plus oil yields obtained under super heated steam (310 bar), where the generated bitumen is favourably cracked to form pyrobitumen (higher residual TOC) and hydrocarbon gas, while under supercritical water conditions (500 and 900 bar), the generated bitumen is favourably cracked to form expelled oil which resulted in less pyrobitumen being formed and lower residual TOCs.

In the case of the vitrinite reflectances (Table 4.4c), similar VR was obtained for both 14 and 25 % TOC source rocks for all experimental conditions under identical time and pressure, indicating both source rocks attaining similar maturities. At 350 °C for 24 h, the VR decreases from 180 bar (1.5 % Ro) to 500 bar (1.0 % Ro). Similarly for the 25 % TOC source rocks, the VR at 180, 500 and 900 bar were 1.5, 0.9, and 0.6 % Ro, respectively. At 420 °C for 24 h, the VR values are relatively higher compared to

experiments conducted at 350 °C due to the increase in temperature. However, lower VR values were obtained from high pressure experiments compared to the low pressure experiments at 420 °C. At 420 °C, the VR for the 14 % TOC source rocks decreases from 2.1 % Ro (310 bar) to 1.7 % Ro (450 bar). In the case of the 25 % TOC source rocks at 420 °C, the VR values at 310, 500 and 900 bar were 2.1, 1.7 and 1.5 % Ro, respectively. The lower VR observed under high water pressure conditions at both 350 and 420 °C for 24 h indicate that water pressure has a retardation effect on source rock maturation. When considering the VR of the initial starting rock (0.4 % Ro on average) for both 14 and 25 % TOC source rocks, the increase in VR at 180, 500 and 900 bar is approx. 1.2, 0.6, and 0.2 % Ro, respectively, at 350 °C. At 420 °C the increase in VR at 310, 500 and 900 bar is approx. 1.7, 1.4, and 1.1 % Ro, where the slightly lower increase in VR at 350 °C shows that the effect of pressure is more pronounced at 350 °C compared to 420 °C.

Table 4.5a and b lists the carbon mass balances from the 14 and 25 % TOC whole rock experiments, respectively. Table 4.5c lists the mean of duplicate results in Table 4.5a and b. In the case of the 14 % TOC source rocks, similar carbon recoveries were obtained at 180 bar (77 %) and 500 bar (79 %) at 350 °C, and at 310 bar (76 %) and 450 bar (73 %) at 420 °C. where the 25 % TOC source rocks also follows the same trend. At 420 °C, the carbon recoveries were slightly lower in comparison to the 350 °C due to more light hydrocarbons being lost during Soxlet extraction and product recovery. Overall, the product recovery (Table 4.5c) from the 14 and 25 % TOC source rocks were good, as the recoveries ranges between 72 to 89 %.

Table 4.4a. Residual rock mass (g) and residual rock TOC (%) and vitrinite reflectance (% Ro) from duplicate experiments (1 and 2) for the whole rock experiments at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Residual rock (g)	Residual rock TOC (%)	Mean VR (% Ro)	Individual reflectance readings (% Ro)
Whole rock	-	-	-		0.3 (4)[b]	0.3, 0.3, 0.3, 0.3
Low pressure 1	180	350	5.9	5.0	1.5 (5)[b]	1.5, 1.6, 1.6, 1.5, 1.5
Low pressure 2	180	350	5.9	5.0	Not Determined	Not Determined
High pressure 1	500	350	5.8	5.0	1.0 (2)[b]	1.0, 1.0
High pressure 2	500	350	5.8	5.2	Not Determined	Not Determined
Low pressure 1	310	420	5.9	8.8	2.0 (4)[b]	2.0, 2.0, 2.0, 2.0
Low pressure 2	310	420	5.9	9.0	Not Determined	Not Determined
High pressure 1	450	420	5.8	7.6	1.70 (2)[b]	1.7, 1.7
High pressure 2	450	420	5.8	7.8	Not Determined	Not Determined

[1 & 2] duplicate runs

[b] values in bracket are the numbers of vitrinite particle measured

Table 4.4b. Residual rock mass (g), residual rock TOC (%) and vitrinite reflectance (% Ro) from duplicate experiments (1 and 2) for the whole rock experiments at 350 and 420 °C for 24 h (25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Residual rock (g)	Residual rock TOC (%)	Mean VR (% Ro)
Whole rock	-	-	-	-	0.4
Low pressure 1	180	350	2.7	14.9	1.5
Low pressure 2	180	350	2.7	14.8	Not Determined
High pressure	500	350	2.7	11.8	0.9
High pressure	900	350	2.7	11.6	0.6
Low pressure 1	310	420	2.9	14.5	2.1
Low pressure 2	310	420	2.9	14.3	Not Determined
High pressure 1	500	420	2.5	11.0	1.7
High pressure 2	900	420	2.5	11.0	1.5

[1 & 2] duplicate runs

[b] values in bracket are the numbers of vitrinite particle measured

Table 4.4c. Mean values from duplicate experiments (1 and 2) for the whole rock experiments at 350 and 420 °C for 24 h in Tables 4.4a and b (14 and 25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Residual rock (g)	Residual rock TOC (%)	Mean VR (% Ro)
Starting rock					
14 % TOC set	-	-	-	14.4	0.3 (4)[b]
25 % TOC set	-	-	-	25.0	0.4
Low pressure					
14 % TOC set	180	350	5.9	5.0	1.5 (5)[b]
25 % TOC set	180	350	2.7	14.8	1.5
High pressure					
14 % TOC set	500	350	5.8	5.1	1.0 (2)[b]
25 % TOC set	500	350	2.8	11.8	0.9
25 % TOC set	900	350	2.7	11.6	0.6
Low pressure					
14 % TOC set	310	420	5.9	8.9	2.0 (4)[b]

Continued					
25 % TOC set	310	420	2.9	14.4	2.1
High pressure					
14 % TOC set	450	420	5.8	7.7	1.7 (2)[b]
25 % TOC set	500	420	2.5	11.1	1.7
25 % TOC set	900	420	2.5	11.0	1.5

[b] values in bracket are the numbers of vitrinite particle measured

Table 4.5a. Carbon mass balance (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the whole rock experiments at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual rock	Total recovered	% recovered
Low pressure 1	180	350	16	451	297	765	77
Low pressure 2	180	350	16	449	293	759	76
High pressure 1	500	350	13	489	289	791	79
High pressure 2	500	350	14	486	285	784	78
Low pressure 1	310	420	148	82	516	747	75
Low pressure 2	310	420	148	78	531	758	76
High pressure 1	450	420	151	129	441	720	72
High pressure 2	450	420	150	126	452	728	73

[1 & 2] duplicate runs

Table 4.5b. Carbon mass balance (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the whole rock experiments at 350 and 420 °C for 24 h (25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual rock	Total recovered	% recovered
Low pressure 1	180	350	31	463	397	891	89
Low pressure 2	180	350	31	458	396	885	88
High pressure	500	350	17	514	327	858	86
High pressure	900	350	12	533	312	856	86
Low pressure 1	310	420	176	122	418	716	72
Low pressure 2	310	420	176	120	412	709	71
High pressure	500	420	143	258	279	680	68
High pressure	900	420	149	271	275	694	69

[1 & 2] duplicate runs

Table 4.5c. Mean values from duplicate experiments (1 and 2) for whole rock experiments at 350 and 420 °C for 24 h in Tables 4.5a and b (14 and 25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual rock	Total recovered	% recovered
Low pressure							
14 % TOC set	180	350	16	450	295	762	77
25 % TOC set	180	350	31	461	397	888	89
High pressure							
14 % TOC set	500	350	14	488	287	788	79
25 % TOC set	500	350	17	514	327	858	86
25 % TOC set	900	350	12	533	312	856	86
Low pressure							
14 % TOC set	310	420	148	80	524	753	76
25 % TOC set	310	420	176	121	415	713	72
High pressure							
14 % TOC set	450	420	151	128	447	724	73

Continued							
25 % TOC set	500	420	143	258	279	680	68
25 % TOC set	900	420	149	271	275	694	69

4.1.4. Main Trends on whole rock experiments.

- The gas yields at 350 °C were reduced, whereas the bitumen plus oil yields increases with increasing water pressure. This is due to the effect of increasing water pressure retarding bitumen cracking to hydrocarbon gas.

- At 420 °C, no pressure effects on gas generation were observed due to similar gas yields generated with increasing water pressure. However, more bitumen plus oil yield is obtained from the high pressure experiments (500 and 900 bar) compared to low pressure (310 bar) due to the supercritical water conditions (present at 500 and 900 bar) favouring the whole rock to generate more expelled oil compared to under superheated steam conditions (present at 310 bar), which favours direct cracking of the whole rock to generate more coke instead of expelled oil.

- Liquid hydrocarbon yields at 350 °C decreases with water pressure, whereas the biomarker ratios indicate a slightly matured bitumen plus oil was obtained from 180 bar compared to 500 bar, indicating pressure retarding effects. In contrast, liquid hydrocarbon yields at 420 °C increases with increasing water pressure due to the increasing aromatic fraction in the bitumen plus oil yields.

- At both 350 and 420 °C, increasing water pressure retards the virtinite reflectance and residual TOC (or coke formation), where the retardation effect of pressure is more pronounced under 350 °C due to the lower temperature conditions compared to 420 °C.

- Under the same experimental conditions, similar vitrinite reflectances were obtained from the 14 and 25 % TOC source rocks. However, the 25 % TOC whole rock generated more hydrocarbon gas and bitumen plus oil due to the higher initial S_2 and HI compared to the 14 % TOC source rocks.

4.2. Bitumen generation experiments.

4.2.1. Gas yields.

The individual and total C_1-C_4 gas yield (mg/g TOC) and gas dryness ratio ($C_1/(C_1$-$C_4)$), from the bitumen generation experiments are listed in Table 4.6a. Table 4.6b lists the mean of the duplicate experiments in Table 4.6a. At 320 °C for 24 h (Table 4.6b), the gas yield was the same with 10 ml (5.1 mg/g TOC) and 15 ml (4.0 mg/g TOC) H_2O. However when comparing the two 15 ml H_2O experiments at 320 °C, the gas yields was only slightly increased from 24 h (4.0 mg/g TOC) to 48 h (6.2 mg/g TOC) due to the doubled residence time.

In order to reduce the experimental time required to reach the point of maximum bitumen generation, the bitumen generation experiments were performed at 340 °C with 10 ml and 15 ml H_2O. The gas yields generated with 15 ml H_2O at 340 °C for 7 h (5.9 mg/g TOC) were the lowest among all of the bitumen generation experiments, whereas a small increase was observed with increasing residence time to 14 h (7.8 mg/g TOC). For experiments conducted at 340 °C for 14 h, a small decrease in gas yield was observed for 10 ml H_2O (9.1 mg/g TOC) compared to using 15 ml H_2O (7.8 mg/g TOC) due to the increase in water to source rock ratio slightly reducing the gas yields (Carr et al., 2009, Uguna et al., 2012a & b). Overall, there is no significant increase in gas yield when the temperature was increased from 320 to 340 °C, as the gas yields generated from the 340 °C bitumen generation experiments are also low and ranges between 6 to 9 mg/g TOC. At 350 °C for 14 h, the experiment generated 9.1 mg/g TOC of hydrocarbon gas, which is similar to the experiments with 10 ml H_2O at 340 °C for 14 h. The gas dryness ratios from the bitumen generation experiments are all similar, ranging from 0.32 to 0.37 for all of the bitumen generation experiments. In conclusion, the low gas yields generated from the bitumen generation experiments (ranging from 4 to 9 mg/g TOC of starting whole rock) indicate that bitumen cracking to hydrocarbon gas were not excessive during these stages of bitumen generation.

Table 4.6a. Individual, total gas (mg/g TOC of starting rock) and gas dryness ratio ($C_1/(C_1\text{-}C_4)$) from duplicate experiments (1 and 2) for bitumen generation experiments (14 % TOC set).

Volume of H_2O (ml)	Experiment (bar)	Temp (°C)	Time (h)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$
10	115-1	320	24	1.72	0.08	1.39	0.19	1.17	0.55	5.1	0.34
10	115-2	320	24	1.80	0.06	1.41	0.17	1.10	0.56	5.1	0.35
15	115-1	320	24	1.39	0.04	1.20	0.11	0.92	0.36	4.0	0.35
15	115-2	320	24	1.41	0.04	1.00	0.12	0.85	0.43	3.9	0.37
15	120-1	320	48	1.99	0.03	1.82	0.11	1.53	0.70	6.2	0.32
15	120-2	320	48	2.09	0.03	1.75	0.10	1.41	0.67	6.1	0.35
15	160-1	340	7	2.14	0.10	1.67	0.20	1.31	0.56	5.9	0.36
15	160-2	340	7	2.13	0.10	1.67	0.20	1.31	0.57	5.9	0.36
10	160-1	340	14	2.94	0.08	2.68	0.35	2.21	0.97	9.2	0.32
10	160-2	340	14	2.89	0.10	2.61	0.21	2.11	0.98	8.9	0.32
15	160-1	340	14	2.63	0.07	2.36	0.19	1.82	0.76	7.8	0.34

Continued											
15	160-2	340	14	2.66	0.05	2.25	0.17	1.89	0.74	7.8	0.34
15	175-1	350	14	2.94	0.05	2.66	0.21	2.22	1.10	9.2	0.32
15	175-2	350	14	2.86	0.05	2.60	0.19	2.17	1.07	9.0	0.32

[1 & 2] duplicate runs

Table 4.6b. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for bitumen generation experiments in Table 4.6a (14 % TOC set).

Volume of H_2O (ml)	Experiment (bar)	Temp (°C)	Time (h)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$
10	115	320	24	1.76	0.07	1.40	0.18	1.14	0.56	5.1	0.35
15	115	320	24	1.40	0.04	1.10	0.12	0.89	0.40	4.0	0.36
15	120	320	48	2.04	0.03	1.79	0.11	1.47	0.69	6.2	0.34
15	160	340	7	2.14	0.10	1.67	0.20	1.31	0.57	6.0	0.36
10	160	340	14	2.92	0.09	2.65	0.28	2.16	0.98	9.1	0.32
15	160	340	14	2.65	0.06	2.31	0.18	1.86	0.75	7.8	0.34
15	175	350	14	2.90	0.05	2.63	0.20	2.20	1.09	9.1	0.32

4.2.2. Bitumen yields.

The bitumen, residual rock mass (g) and residual rock TOC (%) generated from the bitumen generation experiments are listed in Table 4.7a. Table 4.7b lists the mean of duplicate results in Table 4.7a.

At 320 °C for 24 h (Table 4.7b), bitumen yields were 763 and 743 mg/g TOC with 10 ml and 15 ml H_2O, respectively. When comparing the two experiments conducted with 15 ml H_2O at 320 °C, doubling the residence time from 24 to 48 h increases the bitumen yield from 743 to 762 mg/g TOC, which is similar to 10 ml H_2O at 320 °C for 24 h (763 mg/g TOC). At 340 °C, similar amount of bitumen were generated with 15 ml H_2O for 7 h (795 mg/g TOC) and 14 h (786 mg/g TOC), respectively. The experiments conducted with 10 ml H_2O at 340 °C for 14 h (768 mg/g TOC) generated the lowest bitumen yield among the 340 °C experiments. The slightly higher bitumen yields generated with 15 ml H_2O at 340 °C for 7 and 14 h might be due to slight promotional effects of water promoting bitumen generation as stated by Carr et al., (2009) and Uguna et al., (2012a & b).

Figure 4.1 plots the bitumen yield against the bitumen generation experiments, showing the plateau in bitumen yield exists when experiments were conducted at 320 °C for 24 or 48 h and at 340 °C for 7 or 14 h, before the onset of bitumen cracking occurring at 350 °C for 14 h. The bitumen yield at 350 °C for 14 h (661 mg/g TOC) were the lowest among the bitumen generation experiments, indicating that bitumen is cracked into lighter oil and gas at this stage (Table 4.7b). In conclusion, the 15 ml H_2O at 340 °C for 7 h conditions will be chosen as the main bitumen generation experiments due to the shorter experimental time.

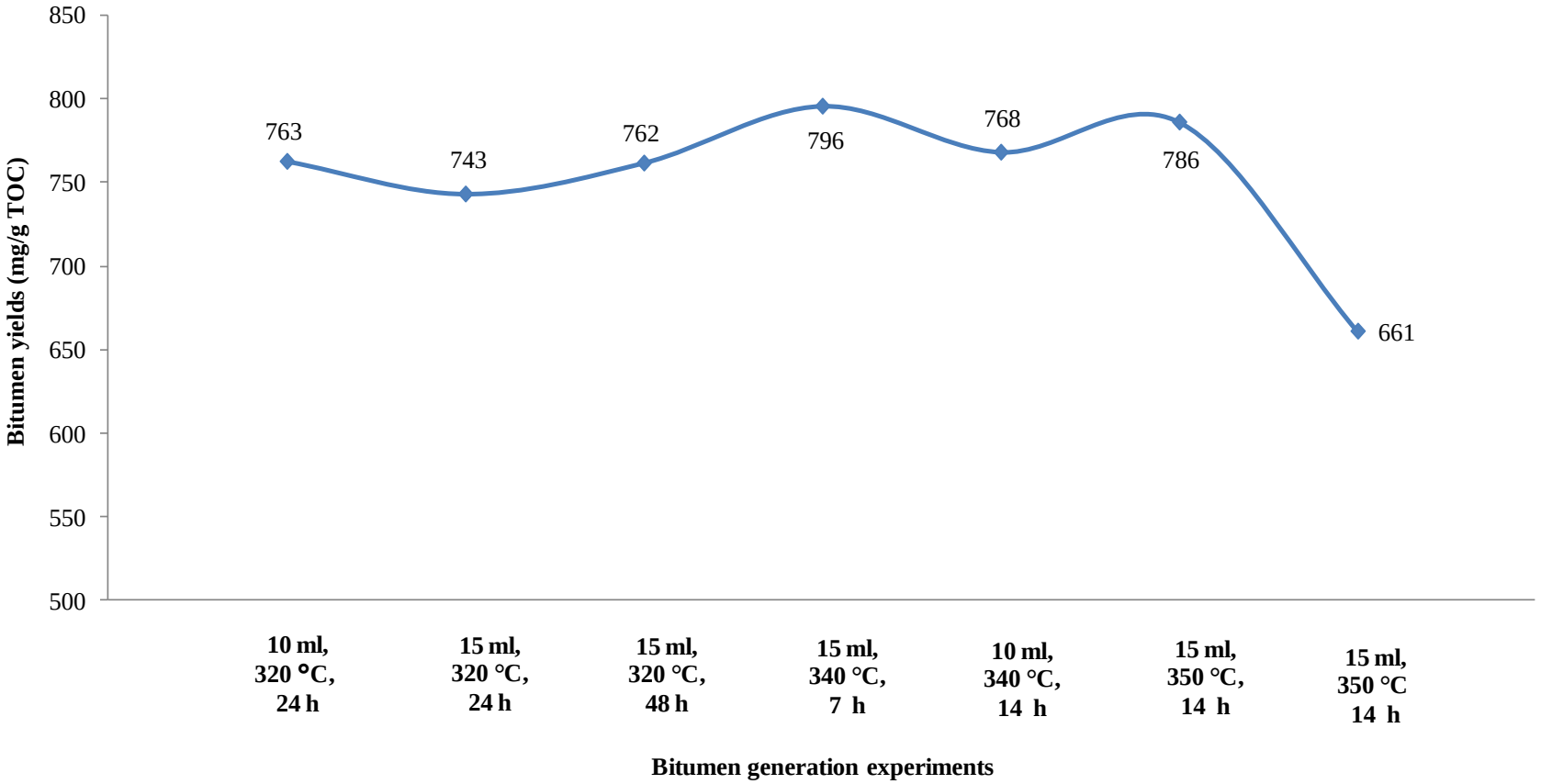


Fig. 4.1. Total bitumen yield against bitumen generation experiments (14 % TOC set).

Table 4.7a. Bitumen plus oil and liquid hydrocarbon yields (mg/g TOC of starting rock), residual rock mass (g) and TOC (%) from duplicate experiments (1 and 2) for bitumen generation experiments (14 % TOC set).

Volume of H_2O	Experiment (bar)	Temp (°C)	Time (h)	Bitumen	Liquid hydrocarbon			Residual Rock (g)	Residual Rock TOC (%)
					Aliphatic	Aromatic	Ali + Aro		
10	115-1	320	24	760	37	66	103	6.0	5.8
10	115-2	320	24	765	39	72	111	5.9	5.8
15	115-1	320	24	738	50	86	136	5.9	5.9
15	115-2	320	24	748	46	88	134	5.9	6.0
15	120-1	320	48	758	53	86	139	5.8	5.2
15	120-2	320	48	765	50	80	130	5.9	5.2
15	160-1	340	7	796	47	86	133	5.8	5.2
15	160-2	340	7	794	47	84	131	5.8	5.2
10	160-1	340	14	765	50	76	126	5.8	4.9
10	160-2	340	14	771	47	73	120	5.8	4.8
15	160-1	340	14	790	55	88	143	5.8	5.5

Continued									
15	160-2	340	14	782	56	92	148	5.8	5.5
15	175-1	350	14	663	91	111	202	5.8	5.3
15	175-2	350	14	659	87	109	196	5.8	5.3

[1 & 2] duplicate runs

Table 4.7b. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for bitumen generation experiments in Table 4.7a (14 % TOC set).

Volume of H_2O	Experiment (bar)	Temp (°C)	Time (h)	Bitumen	Liquid hydrocarbon			Residual Rock (g)	Residual Rock TOC (%)
					Aliphatic	Aromatic	Ali + Aro		
10	115	320	24	763	38	69	107	6.0	5.8
15	115	320	24	743	48	87	135	5.9	6.0
15	120	320	48	762	52	83	135	5.8	5.2
15	160	340	7	795	47	85	132	5.8	5.2
10	160	340	14	768	49	75	123	5.8	4.8
15	160	340	14	786	56	90	146	5.8	5.5
15	175	350	14	661	89	110	199	5.8	5.3

4.2.3 Residual TOC and carbon mass balances.

At 320 °C for 24 h (Table 4.7b), similar residual TOC were generated with 10 ml (5.8 % TOC) and 15 ml (6.0 % TOC) H_2O. However at 320 °C for 48 h, the residual TOC is slightly reduced to 5.2 % TOC. This is consistent with the slightly higher bitumen yields generated for 48 h compared to 24 h with 15 ml H_2O at 320 °C. At 340 °C, the experiments conducted with 10 ml H_2O for 14 h generates the lowest residual TOC value (4.8 % TOC). For experiments conducted with 15 ml H_2O at 340 °C, similar residual TOC were generated for 7 h (5.2 % TOC) and 14 h (5.5 % TOC). At 350 °C for 14 h, the residual TOC is 5.3 % TOC, which is similar to the experiments conducted at 340 °C for 7 and 14 h. Apart from the slightly lower residual TOC value at 340 °C 10 ml H_2O for 14 h (4.8 % TOC), similar residual TOCs were generated throughout the rest of the bitumen generation experiments.

Table 4.8 lists the carbon mass balances from the bitumen generation experiments. The carbon recovery was ≥ 90 %, except for the experiment at 350 °C for 14 h which only showed a carbon recovery of 85 %. The lower carbon recovery at 350 °C is expected due to lighter hydrocarbons being loss during drying of the pyrolysed rock (prior to Soxhlet extraction) and Soxhlet extraction compared to the bitumen generation experiments at 320 and 340 °C. High carbon recoveries (≥ 90 %) from the remaining experiments indicate that product recovery were good for all bitumen generation experiments. High recoveries (≥ 90 %) were also determined from the bitumen generation experiments from the 25 and 30 % TOC source rocks (350 °C for 6 h).

The series of bitumen generation experiments conducted on the 14, 25 and 30 % TOC source rocks are presented in Table 4.9a, b & c, respectively. The 25 and 30 % TOC bitumen generation experiments were all conducted at 350 °C for 6 h at 180 bar under low hydrous pressure conditions.

Table 4.8. Carbon mass balance from duplicate experiments (1 and 2) for bitumen generation experiments (14 % TOC set).

Volume of H_2O (ml)	Experiment (bar)	Temp (°C)	Time (h)	Total (C_1-C_4)	Bitumen	Residual Rock (g)	Total recovered	% recovered
10	115-1	320	24	4	608	344	957	96
10	115-2	320	24	4	612	345	961	96
15	115-1	320	24	3	590	351	945	95
15	115-2	320	24	3	598	356	957	96
15	120-1	320	48	5	606	301	913	91
15	120-2	320	48	5	612	305	922	92
15	160-1	340	7	5	637	303	944	94
15	160-2	340	7	5	635	302	942	94
10	160-1	340	14	7	612	283	902	90
10	160-2	340	14	7	617	278	902	90
15	160-1	340	14	6	632	322	961	96

Continued								
15	160-2	340	14	6	626	321	953	95
15	175-1	350	14	7	530	308	846	85
15	175-2	350	14	7	527	307	841	84

[1 & 2] duplicate runs

Table 4.9a. Individual and total gas (mg/g of TOC of starting rock), gas dryness ratio ($C_1/(C_1\text{-}C_4)$), bitumen yields (mg/g of TOC of starting rock), residual rock mass (g), residual rock TOC (%) and mean values for the bitumen and partially matured source rock generation experiments (14 % TOC set).

Experiment (bar)	Temp (°C)	Time (h)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	Bitumen	Residual Rock (g)	Residual Rock TOC (%)
160-1	340	7	2.08	0.09	1.66	0.20	1.33	0.6	6.0	0.35	797	5.8	5.2
160-2	340	7	1.99	0.07	1.58	0.16	1.13	0.41	5.3	0.37	799	5.8	5.2
160-3	340	7	2.11	0.12	1.57	0.25	1.29	0.50	5.8	0.36	790	5.8	5.2
160-4	340	7	2.08	0.10	1.66	0.21	1.31	0.52	5.9	0.35	802	5.8	5.2
160-5	340	7	2.00	0.10	1.73	0.18	1.29	0.52	5.8	0.34	791	5.8	5.2
160-6	340	7	1.95	0.08	1.63	0.22	1.33	0.58	5.8	0.34	796	5.8	5.2
160-7	340	7	2.18	0.09	1.68	0.2	1.42	0.61	6.2	0.35	779	5.8	5.2
160-8	340	7	2.09	0.09	1.68	0.19	1.31	0.55	5.9	0.35	805	5.8	5.2
160-9	340	7	2.06	0.08	1.67	0.34	1.46	0.55	6.2	0.33	785	5.8	5.2
160-10	340	7	2.17	0.09	1.62	0.18	1.37	0.54	6.0	0.36	792	5.8	5.2

Continued													
160-11	340	7	2.18	0.1	1.69	0.17	1.01	0.52	5.7	0.38	801	5.8	5.3
160-12	340	7	2.14	0.09	1.65	0.18	1.29	0.55	5.9	0.36	820	5.8	5.2
160-13	340	7	2.21	0.09	1.61	0.33	1.39	0.54	6.2	0.36	789	5.8	5.2
160-14	340	7	2.09	0.09	1.56	0.19	1.26	0.54	5.7	0.36	787	5.8	5.2
160-15	340	7	2.17	0.12	1.59	0.19	1.32	0.55	5.9	0.37	805	5.8	5.2
160-16	340	7	2.11	0.10	1.66	0.21	1.31	0.59	6.0	0.35	782	5.8	5.2
Mean values			2.10	0.09	1.64	0.21	1.30	0.54	5.9	0.36	795	5.8	5.2

Table 4.9b. Individual and total gas (mg/g of TOC of starting rock), gas dryness ratio ($C_1/(C_1\text{-}C_4)$), bitumen yields (mg/g of TOC of starting rock), residual rock mass (g), residual rock TOC (%) and mean values for the bitumen and partially matured source rock generation experiments (25 % TOC set).

Experiment (bar)	Temp (°C)	Time (h)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	Bitumen	Residual Rock (g)	Residual Rock TOC (%)
180-1	350	6	5.27	0.27	4.65	0.64	3.42	1.64	16	0.33	962	2.5	6.2
180-2	350	6	5.11	0.23	4.57	0.62	3.44	1.68	16	0.33	954	2.5	6.2
180-3	350	6	5.25	0.25	4.71	0.63	3.56	1.71	16	0.33	952	2.5	6.2
180-4	350	6	5.22	0.24	4.55	0.58	3.37	1.58	16	0.34	957	2.5	6.0
180-5	350	6	5.31	0.26	4.70	0.70	3.54	1.70	16	0.33	953	2.5	6.2
180-6	350	6	5.35	0.26	4.66	0.60	3.42	1.68	16	0.34	941	2.5	6.2
180-7	350	6	5.26	0.25	4.65	0.64	3.43	1.69	16	0.33	954	2.5	6.2
180-8	350	6	5.26	0.25	4.65	0.64	3.43	1.69	16	0.33	954	2.5	6.2
Mean values			5.25	0.25	4.64	0.63	3.45	1.67	16	0.33	953	2.5	6.2

Table 4.9c. Individual and total gas (mg/g of TOC of starting rock), gas dryness ratio ($C_1/(C_1-C_4)$), bitumen yields (mg/g of TOC of starting rock), residual rock mass (g), residual rock TOC (%) and mean values for the bitumen and partially matured source rock generation experiments (30 % TOC set).

Experiment (bar)	Temp (°C)	Time (h)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1-C_4)}$	Bitumen	Residual Rock (g)	Residual Rock TOC (%)
180-1	350	6	4.05	0.17	3.43	0.39	2.53	1.18	12	0.35	948	1.9	9.2
180-2	350	6	3.89	0.17	3.47	0.41	2.55	1.20	12	0.33	950	1.9	9.1
180-3	350	6	3.72	0.16	3.31	0.39	2.45	1.17	11	0.33	951	1.9	9.1
180-4	350	6	3.73	0.16	3.32	0.38	2.46	1.15	11	0.33	952	1.9	9.2
Mean values			3.85	0.17	3.38	0.39	2.50	1.18	12	0.34	950	1.94	9.2

4.2.4. Main trends on bitumen generation experiments.

- The low gas yields indicate that the point of excessive bitumen cracking is not reached for all the bitumen generation experiments.

- The plateau in bitumen yield from the 14 % TOC source rocks exists when experiments were conducted at 320 °C for 24 or 48 h and at 340 °C for 7 or 14 h before the onset of bitumen cracking. The 15 ml H_2O at 340 °C for 7 h experiment will be chosen as the main 14 % TOC bitumen generation experiment due to shorter residence time.

4.3. Isolated partially matured source rock experiments.

4.3.1. Gas yields.

The individual and total C_1-C_4 gas yield (mg/g TOC) and gas dryness ratio ($C_1/(C_1$-$C_4)$), generated from the isolated partially matured source rock at 350 and 420 °C for 24 h are listed in Tables 4.10a and b, respectively. Table 4.10c lists the mean of duplicate results in Tables 4.10a and b. The Rock Eval data (S_2, HI and T_{max}) from the residual 14 and 25 % TOC isolated partially matured source rocks are listed in Tables 4.11a and b, respectively.

At 350 °C for 24 h (Table 4.10c), the total gas yield from the 14 % TOC partially matured source rock was highest at 180 bar (3.1 mg/g TOC) and reduced by half at 500 bar (1.2 mg/g TOC). The 25 % TOC source rocks also follows the same trend at 350 °C where the total gas yields at 180, 500 and 900 bar are 1.0, 0.49 and 0.35 mg/g TOC, respectively. When the temperature was increased to 420 °C for 24 h, a significant increase in gas yield was observed for both low (310 bar) and high pressure (450 bar) experiments due to the severe cracking of the partially matured source rock at higher temperature compared to 350 °C. At 420 °C for 24 h (Table 4.10c), the gas yields generated from the 14 % TOC source rocks at 310 (23 mg/g TOC) and 450 bar (23 mg/g TOC) is the same. The 25 % TOC source rocks follows the same trend where similar gas yields were generated at 310 bar (9.0 mg/g TOC), 500 bar (7.0 mg/g TOC) and 900 bar (6.0 mg/g TOC) at 420 °C for 24 h. The gas dryness ratios at 350 and 420 °C for 24 h (Table 4.10c) shows that the hydrocarbon gases was slightly dryer from the high pressure experiments as opposed to their corresponding low pressure experiments, indicating slightly more methane were generated in relation to the other hydrocarbon gases as pressure was increased. For both source rocks, at 350 °C the gas dryness ratio increases from approx. 0.37 to 0.46 at 180 and 900 bar, respectively, whereas at 420 °C the gas dryness ratio increases from approx. 0.46 to 0.52 at 310 and 900 bar, respectively.

At 350 °C, the S_2 value from the 14 % TOC source rocks at 180 bar (1.2 mg/g TOC) is lower than at 500 bar (2.7 mg/g TOC). Similarly, the S_2 from the 25 % TOC source rocks at 180, 500 and 900 bar is 1.0, 1.5 and 2.0 mg/g TOC, respectively at 350 °C. The decrease in gas yields is consistent with increasing S_2 value, indicating that under high pressure (500 and 900 bar), more hydrocarbon generating potential remains in the residual rock due to pressure retarding gas generation for the isolated partially matured source rock. The lower S_2 values at 420 °C compared to 350 °C indicates that due to the severe cracking at 420 °C, the hydrocarbon potential remaining from the residual rocks were much less. The S_2 from the 14 % TOC source rocks also follows the same trend as the gas yields, where similar values were obtained at 310 bar (0.1 mg/g TOC) and 450 bar (0.2 mg/g TOC) at 420 °C. The S_2 from the 25 % TOC source rocks also shows the same trend as the gas yields, where similar S_2 values were obtained from 310 bar (0.3 mg/g TOC), 500 bar (0.2 mg/g TOC) and 900 bar (0.2 mg/g TOC) bar. Due to the slightly higher initial S_2 (9.3 mg/g TOC) and higher initial HI (179 mg/g TOC) from the 14 % TOC partially matured source rock compared to the 25 % TOC partially matured source rock (where the S_2 and HI shows a value of 7.0 and 114 mg/g TOC, respectively) the gas yield generated from the 14 % TOC source rocks are always higher under all experimental conditions.

Overall, the 14 and 25 % TOC partially matured source rocks follow the same gas yield trends as those for whole rocks (Section 4.1.1), where pressure retarding effects were observed at 350 °C due to the increasing water pressure retarding hydrocarbon gas generation, whereas leveled gas yields were observed at 420 °C for 24 h due to the applied water pressure being insufficient to retard gas generation, and is consistent with the studies conducted by Uguna et al., (2012a & b) mentioned previously.

Table 4.10a. Individual and total gas (mg/g TOC of starting rock), gas dryness ratio ($C_1/(C_1\text{-}C_4)$), and alkene/alkane (C_2H_4/C_2H_6; C_3H_6/C_3H_8) ratios from duplicate experiments (1 and 2) for the partially matured source rock pyrolysed individually at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	$\frac{C_2H_4}{C_2H_6}$	$\frac{C_3H_6}{C_3H_8}$
Low pressure 1	180	350	0.98	0.02	0.91	0.10	0.64	0.41	3.0	0.33	0.022	0.156
Low pressure 2	180	350	1.01	0.03	0.90	0.11	0.70	0.34	3.1	0.32	0.033	0.157
High pressure 1	500	350	0.40	0.01	0.30	0.01	0.22	0.12	1.1	0.38	0.033	0.045
High pressure 2	500	350	0.44	0.01	0.31	0.01	0.27	0.11	1.2	0.38	0.032	0.037
Low pressure 1	310	420	10.5	0.01	5.18	0.04	4.91	2.17	23	0.46	0.002	0.008
Low pressure 2	310	420	9.43	0.02	5.35	0.06	4.82	2.13	22	0.43	0.004	0.012
High pressure 1	450	420	9.84	0.01	5.67	0.04	4.99	2.29	23	0.43	0.002	0.008
High pressure 2	450	420	9.44	0.01	5.40	0.04	4.88	2.24	22	0.43	0.002	0.008

[1 & 2] duplicate runs

Table 4.10b. Individual and total gas (mg/g TOC of starting rock), gas dryness ratio ($C_1/(C_1\text{-}C_4)$), and alkene/alkane (C_2H_4/C_2H_6; C_3H_6/C_3H_8) ratios from duplicate experiments (1 and 2) for the partially matured source rock pyrolysed individually at 350 and 420 °C for 24 h (25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	$\frac{C_2H_4}{C_2H_6}$	$\frac{C_3H_6}{C_3H_8}$
Low pressure 1	180	350	0.39	0.01	0.28	0.04	0.18	0.10	1.0	0.39	0.036	0.222
Low pressure 2	180	350	0.40	0.01	0.24	0.05	0.19	0.10	0.99	0.40	0.042	0.263
High pressure	500	350	0.19	0.00	0.13	0.01	0.10	0.06	0.49	0.39	0.000	0.100
High pressure	900	350	0.16	0.00	0.08	0.00	0.06	0.04	0.35	0.46	0.000	0.000
Low pressure 1	310	420	4.00	0.02	2.05	0.05	1.60	0.84	9	0.47	0.010	0.031
Low pressure 2	310	420	4.09	0.01	2.06	0.03	1.61	0.83	9	0.47	0.005	0.019
High pressure	500	420	3.60	0.01	1.57	0.02	1.19	0.62	7	0.51	0.006	0.017
High pressure	900	420	2.94	0.00	1.27	0.01	0.98	0.51	6	0.52	0.000	0.010

[1 & 2] duplicate runs

Table 4.10c. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the partially matured source rock pyrolysed individually in Table 4.10a and b (14 and 25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	$\frac{C_2H_4}{C_2H_6}$	$\frac{C_3H_6}{C_3H_8}$
Low pressure												
14 % TOC set	180	350	1.00	0.03	0.91	0.11	0.67	0.38	3.1	0.33	0.033	0.164
25 % TOC set	180	350	0.40	0.01	0.26	0.05	0.19	0.10	1.0	0.40	0.038	0.263
High pressure												
14 % TOC set	500	350	0.42	0.01	0.31	0.01	0.25	0.12	1.2	0.38	0.032	0.040
25 % TOC set	500	350	0.19	0.00	0.13	0.01	0.10	0.06	0.49	0.39	0.000	0.100
25 % TOC set	900	350	0.16	0.00	0.08	0.00	0.06	0.04	0.35	0.46	0.000	0.000
Low pressure												
14 % TOC set	310	420	9.97	0.02	5.27	0.05	4.87	2.15	23	0.45	0.004	0.010
25 % TOC set	310	420	4.05	0.02	2.06	0.04	1.61	0.84	9	0.47	0.010	0.025
High pressure												
14 % TOC set	450	420	9.64	0.01	5.54	0.04	4.94	2.27	23	0.43	0.002	0.008

Continued												
25 % TOC set	500	420	3.60	0.01	1.57	0.02	1.19	0.62	7	0.51	0.006	0.017
25 % TOC set	900	420	2.94	0.00	1.27	0.01	0.98	0.51	6	0.52	0.000	0.010

Table 4.11a. Rock Eval Data (S_2, HI and T_{max}) for the 14 % TOC set isolated partially matured source rock experiments at 350 and 420 °C for 24 h (14 %TOC set).

Experiment	Pressure (bar)	Temp (°C)	Time (h)	S_2 (mg/g TOC)	HI (mg/g TOC)	T_{max} (°C)
Bitumen Generation	160	340	7	9.3	179	438
Low pressure	180	350	24	1.2	30	445
High pressure	500	350	24	2.7	64	447
Low pressure	310	420	24	0.1	3	605
High pressure	450	420	24	0.2	4	606

Table 4.11b. Rock Eval Data (S_2, HI and T_{max}) for the 25 % TOC set isolated partially matured source rock experiments at 350 and 420 °C for 24 h (25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Time (h)	S_2 (mg/g TOC)	HI (mg/g TOC)	T_{max} (°C)
Bitumen Generation	180	350	6	7.0	114	436
Low pressure	180	350	24	1.0	22	446
High pressure	500	350	24	1.5	35	442
High pressure	900	350	24	2.0	35	446
Low pressure	310	420	24	0.3	7	596
High pressure	500	420	24	0.2	3	599
High pressure	900	420	24	0.2	3	601

4.3.2. Bitumen plus oil yields.

Table 4.12a and b lists the bitumen plus oil yields (mg/g TOC) generated from 14 and 25 % TOC isolated partially matured source rock, respectively. Table 4.12c lists the mean of duplicate results in Table 4.12a and b.

At 350 °C for 24 h (Table 4.12c), the bitumen plus oil yield from the 14 % TOC source rocks was slightly increased from 180 bar (40 mg/g TOC) to 500 bar (52 mg/g TOC), whereas the similar amounts were generated from the 25 % TOC source rocks at 180 bar (15 mg/g TOC), 500 bar (15 mg/g TOC) and 900 bar (13 mg/g TOC). At 420 °C for 24 h, bitumen plus oil yield from the 14 % TOC source rocks was also increased going from 180 bar (12 mg/g TOC) to 500 bar (26 mg/g TOC). As for the 25 % TOC source rocks at 420 °C, the bitumen plus oil yields decreases at 310 bar (31 mg/g TOC) to 500 bar (11 mg/g TOC) and 900 bar (10 mg/g TOC). The bitumen plus oil yields generated from 14 % TOC source rocks were slightly higher compared to the 25 % TOC source rocks for all experimental conditions due to the higher initial S_2 of the 14 % TOC source rocks, apart from experiments at 310 bar and 420 °C for 24 h. This might be due to the slightly lower S_2 (0.1 mg/g TOC) from the 14 % TOC source rocks compared to the 25 % TOC source rocks (0.3 mg/g TOC) at 310 bar and 420 °C, indicating that there is less hydrocarbon generating potential remaining in the residual 14 % TOC source rocks compared to the 25 % TOC source rocks.

Overall, the bitumen plus oil yield generated from the 14 % TOC partially matured source rocks follow the same trends as those for whole rocks (Section 4.1.2), where more bitumen plus oil yield were generated from the higher pressure experiments (500 and 450 bar) compared to the low pressure experiments (180 and 310 bar) at both 350 and 420 °C. However, in the case of the 25 % TOC source rocks, no significant pressure effects were observed on the bitumen plus oil yield at 350 °C, whereas at 420 °C the amount of bitumen plus oil yields decreases with increasing water pressure, which is in contrast to those observed for whole rock.

Table 4.12a. Bitumen plus oil yields (mg/g TOC) from duplicate experiments (1 and 2) for the partially matured source rock pyrolysed individually at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Bitumen plus oil
Low pressure 1	180	24	350	42
Low pressure 2	180	24	350	38
High pressure 1	500	24	350	49
High pressure 2	500	24	350	54
Low pressure 1	310	24	420	12
Low pressure 2	310	24	420	12
High pressure 1	450	24	420	28
High pressure 2	450	24	420	24

[1 & 2] duplicate runs

Table 4.12b. Bitumen plus oil yields (mg/g TOC) from duplicate experiments (1 and 2) for the partially matured source rock pyrolysed individually at 350 and 420 °C for 24 h (25 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Bitumen plus oil
Low pressure 1	180	24	350	14
Low pressure 2	180	24	350	15
High pressure	500	24	350	15
High pressure	900	24	350	13
Low pressure 1	310	24	420	30
Low pressure 2	310	24	420	32
High pressure	500	24	420	11
High pressure	900	24	420	12

[1 & 2] duplicate runs

Table 4.12c. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the partially matured source rock pyrolysed individually in Table 4.12a and b (14 and 25 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Bitumen plus oil
Low pressure				
14 % TOC set	180	24	350	40
25 % TOC set	180	24	350	15
High pressure				
14 % TOC set	500	24	350	52
25 % TOC set	500	24	350	15
25 % TOC set	900	24	350	13
Low pressure				
14 % TOC set	310	24	420	12
25 % TOC set	310	24	420	31

Continued				
High pressure				
14 % TOC set	450	24	420	26
25 % TOC set	500	24	420	11
25 % TOC set	900	24	420	12

4.3.3. Residual TOC, vitrinite reflectance (VR) and carbon mass balances.

The residual rock mass (g), residual rock TOC (%) and vitrinite reflectance (% Ro) for the partially matured source rock experiments at 350 and 420 °C for 24 h from the 14 and 25 % TOC source rocks are listed in Tables 4.13a and b, respectively. Table 4.13c lists the mean of duplicate results in Tables 4.13a and b at 350 °C, whereas Table 4.13d lists the mean of duplicate results in Table 4.13a and b at 420 °C.

At 350 °C for 24 h (Table 4.13c), the residual TOC from the 14 % TOC source rocks at 180 bar (4.0 % TOC) and 500 bar (4.2 % TOC) were similar. The 25 % TOC source rocks also follows the same trend where similar residual TOC were generated at 180 bar (4.5 % TOC) and 500 bar (4.4 % TOC), apart from 900 bar (5.7 % TOC) where the residual TOC is slightly higher compared to 180 and 500 bar. At 420 °C for 24 h (Table 4.13c), similar TOC yields were generated from the 14 % TOC source rocks at 310 bar (4.5 % TOC) and 450 bar (4.7 % TOC). The 25 % TOC source rocks also shows the same trend where the TOC yields obtained at 310, 500 and 900 bar were 4.4, 4.7 and 5.0 % TOC, respectively.

At 350 °C for 24 h (Table 4.13c), the VR from the 14 % TOC source rocks decreases from 180 bar (1.3 % Ro) to 500 bar (0.9 % Ro). The same trend is also shown at 420 °C (Table 4.13d), where the VR decreases from 310 bar (1.8 % Ro) to 450 bar (1.5 % Ro). The lower VR observed under high water pressure conditions at both 350 and 420 °C for 24 h indicates that water pressure has a retardation effect on source rock maturation. When considering the VR of the initial starting rock (0.9 % Ro), the increase in VR at 180 and 500 bar is 0.47 % Ro and 0.0 % Ro, respectively, at 350 °C, whereas at 420 °C the increase in VR at 310 and 450 bar is 0.9 % Ro and 0.7 % Ro, respectively where the slightly lower increase in VR at 350 °C shows that the effect of pressure is more pronounced at 350 °C compared to 420 °C. This is especially true at 350 °C and 500 bar where the VR value was similar to the initial partially matured rock (0.9 % Ro).

At 350 °C, the 14 % TOC source rocks shows higher S_2 value at 500 bar (2.7 mg/g TOC) compared to 180 bar (1.2 mg/g TOC). The 25 % TOC source rocks also follows the same trend where the highest S_2 value were obtained at 900 bar (2.0 mg/g TOC) compared to 500 bar (1.6 mg/g TOC) and 180 bar (1.0 mg/g TOC) showing that there is slightly more hydrocarbon generating potential remaining in the residual rock at 900 bar. The T_{max} values for both source rocks at 350 °C were similar at all pressures ranging between 442-447 °C. The same trend follows at 420 °C, where similar T_{max} values were also obtained, ranging from 596-606 °C at all pressures. The lower HI and higher T_{max} at 420 °C also indicate that the residual rocks were more matured compared to 350 °C.

Table 4.14a & b lists the carbon mass balances from the 14 and 25 % TOC partially matured source rock experiments, respectively. Slightly higher recoveries were obtained from the 14 % source rocks compared to the 25 % TOC source rocks under all experimental conditions. For both source rocks, the carbon recoveries were higher from high pressure experiments compared to the low pressure experiments at 350 and 420 °C due to more light hydrocarbons from the bitumen plus oil generated at low pressure being lost during Soxlet extraction and product recovery. Overall, high recoveries were determined from the partially matured source rock experiments, ranging from 73 to 99 %.

Table 4.13a. Residual rock mass (g), residual rock TOC (%) and vitrinite reflectance (% Ro) from duplicate experiments (1 and 2) for the partially matured source rock pyrolysed individually at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Residual Rock (g)	Residual rock TOC (%)	Mean VR (% Ro)	Individual reflectance readings (% Ro)
Bitumen generation	160	7	340	5.8	5.2	0.9 (6)[b]	0.8, 0.8, 0.8, 0.9, 0.9, 0.9
Low pressure 1	180	24	350	5.7	3.9	1.3 (3)[b]	1.4, 1.3, 1.3
Low pressure 2	180	24	350	5.7	4.0		
High pressure 1	500	24	350	5.7	4.2	0.9 (3)[b]	0.8, 0.9, 0.9
High pressure 2	500	24	350	5.6	4.3		
Low pressure 1	310	24	420	5.6	4.5	1.8 (2)[b]	1.7, 1.8
Low pressure 2	310	24	420	5.5	4.5		
High pressure 1	450	24	420	5.5	4.7	1.5 (4)[b]	1.5, 1.5, 1.6, 1.6
High pressure 2	450	24	420	5.5	4.7		

[1 & 2] duplicate runs

[b] values in bracket are the numbers of vitrinite particle measured

Table 4.13b. Residual rock mass (g) and residual rock TOC (%) from duplicate experiments (1 and 2) for the partially matured source rock pyrolysed individually at 350 and 420 °C for 24 h (25 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Residual Rock (g)	Residual rock TOC (%)
Bitumen generation	160	6	350	2.5	6.2
Low pressure 1	180	24	350	2.3	4.5
Low pressure 2	180	24	350	2.3	4.5
High pressure	500	24	350	2.3	4.4
High pressure	900	24	350	2.4	5.7
Low pressure 1	310	24	420	2.3	4.4
Low pressure 2	310	24	420	2.3	4.3
High pressure	500	24	420	2.2	4.7
High pressure	900	24	420	2.1	5.0

[1 & 2] duplicate runs

Table 4.13c. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the partially matured source rock pyrolysed individually at 350 °C for 24 h in Table 4.13a and b (14 and 25 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Residual Rock (g)	Residual rock TOC (%)	Mean VR (% Ro)	Individual reflectance readings (% Ro)
Bitumen generation							
14 % TOC set	160	7	340	5.8	5.2	0.9 (6)[b]	0.8, 0.8, 0.8, 0.9, 0.9, 0.9
25 % TOC set	160	6	350	2.5	6.2		Not determined
Low pressure							
14 % TOC set	180	24	350	5.6	4.0	1.3 (3)[b]	1.4, 1.3, 1.3
25 % TOC set	180	24	350	2.3	4.5		Not determined
High pressure							
14 % TOC set	500	24	350	5.7	4.2	0.9 (3)[b]	0.8, 0.9, 0.9
25 % TOC set	500	24	350	2.3	4.4		Not determined
25 % TOC set	900	24	350	2.4	5.7		

[b] values in bracket are the numbers of vitrinite particle measured

Table 4.13d. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the partially matured source rock pyrolysed individually at 420 °C for 24 h in Table 4.13a and b (14 and 25 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Residual Rock (g)	Residual rock TOC (%)	Mean VR (% Ro)	Individual reflectance readings (% Ro)
Bitumen generation							
14 % TOC set	160	7	340	5.8	5.2	0.9 (6)[b]	0.8, 0.8, 0.8, 0.9, 0.9, 0.9
25 % TOC set	160	6	350	2.5	6.2		Not determined
Low pressure							
14 % TOC set	310	24	420	5.6	4.5	1.8 (2)[b]	1.7, 1.8
25 % TOC set	310	24	420	2.3	4.4		Not determined
High pressure							
14 % TOC set	450	24	420	5.6	4.7	1.5 (4)[b]	1.5, 1.5, 1.6, 1.6
25 % TOC set	500	24	420	2.2	4.7		Not determined
25 % TOC set	900	24	420	2.1	5.0		

[b] values in bracket are the numbers of vitrinite particle measured

Table 4.14a. Carbon mass balance from duplicate experiments (1 and 2) for the partially matured source rock pyrolysed individually at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual Rock	Total recovered	% recovered
Low pressure 1	180	350	2.4	34	221	257	85
Low pressure 2	180	350	2.6	30	226	259	85
High pressure 1	500	350	0.8	39	236	276	91
High pressure 2	500	350	0.9	43	243	287	95
Low pressure 1	310	420	18	10	251	279	93
Low pressure 2	310	420	17	10	249	276	92
High pressure 1	450	420	18	22	258	298	99
High pressure 2	450	420	17	19	255	292	97

[1 & 2] duplicate runs

Table 4.14b. Carbon mass balance from duplicate experiments (1 and 2) for the partially matured source rock pyrolysed individually at 350 and 420 °C for 24 h (25 % TOC set).

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Experiment	Pressure (bar)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual Rock	Total recovered	% recovered
Low pressure 1	180	350	0.79	10	102	113	73
Low pressure 2	180	350	0.78	15	101	117	76
High pressure	500	350	0.38	12	101	113	75
High pressure	900	350	0.28	10	137	147	99
Low pressure 1	310	420	7	24	101	131	86
Low pressure 2	310	420	7	26	99	132	86
High pressure	500	420	5.45	8	104	117	77
High pressure	900	420	4.44	10	105	119	78

[1 & 2] duplicate runs

4.3.4. Main trends on partially matured source rock experiments.

- Despite the hydrocarbon generating potential of the partially matured source rocks being very low compared to the whole rock experiments, the gas yields behave similarly to whole rocks where at 350 °C, hydrocarbon gases are reduced with increasing water pressure, and no pressure effects were observed at 420 °C due to similar gas yields with increasing water pressure.

- The S_2 value of the residual partially matured source rocks also reflects the gas yield trends, where S_2 value increases with water pressure at 350 °C, whereas at 420 °C the S_2 values are similar for all pressures.

- For both 14 and 25 % TOC partially matured source rocks, no significant change in bitumen plus oil yield and residual TOC were observed with increasing water pressure at 350 °C for 24 h. However, at 420 °C bitumen plus oil yields generated from the 14 % TOC partially matured source rocks increases with water pressure, whereas a reverse trend was observed from the 25 % TOC partially matured source rocks, where the bitumen plus oil yields decreases with water pressure.

- The VR from the 14 % TOC source rocks decreases with increasing water pressure at both 350 and 420 °C, where the effect of pressure is also more pronounced at 350 °C.

4.4. Isolated bitumen cracking experiments.

4.4.1. Gas yields.

The individual and total C_1-C_4 gas yield (mg/g TOC of starting rock), gas dryness ratio ($C_1/(C_1$-$C_4)$), and alkene/alkane gas ratios generated for the isolated bitumen cracking experiments at 350 and 420 °C for 24 h are listed in Tables 4.15a and b, from the 14 and 25 % TOC bitumen, respectively. Table 4.15c lists the mean of duplicate results in Table 4.15a and b for both bitumens at 350 °C, whereas Table 4.15d lists the mean of duplicate results in Table 4.15a and b for both bitumens at 420 °C.

At 350 °C for 24 h (Table 4.15c), the total gas yield from the 14 % TOC bitumen were highest at 180 bar (9 mg/g TOC) and reduced at 500 bar (3.6 mg/g TOC). The 25 % TOC bitumen also follows the same trend at 350 °C where the total gas yields at 180, 500 and 900 bar is 10, 4.3 and 2.6 mg/g TOC, respectively. This is due to water pressure retarding bitumen cracking to gas which is consistent with the previous studies (Carr et al., 2009; Uguna et al., 2012a & b). At 420 °C for 24 h, when pressure increases from 310 to 450 bar, there is no significant difference in gas yield observed from the 14 % TOC bitumen (90 and 88 mg/g TOC at 310 and 450 bar, respectively). The 25 % TOC bitumen also shows the same trend where similar gas yields were generated at 310 bar (107 mg/g TOC) and 500 bar (97 mg/g TOC), whereas slightly higher gas yields were generated at 900 bar (119 mg/g TOC) at 420 °C for 24 h. Overall, leveled gas yields were also observed for bitumen cracking under all experimental conditions at 420 °C from the 14 and 25 % TOC bitumen due to water promotional effects being more dominant over the effects of water pressure compared to the temperature at 350 °C, as interpreted by Uguna et al., (2012a & b).

Isolated bitumen cracking experiments from the 14 % TOC bitumen were also conducted at 420 °C under anhydrous (25 bar) and high water pressure (450 bar) conditions in the presence and absence of montmorillonite clay (Table 4.15a and d). In the absence of montmorillonite clay, the gas yields generated from the anhydrous

experiments (65 mg/g TOC) were lower in comparison to the 310 bar experiments (90 mg/g TOC). This is due to the effects of water promoting gas generation at the 310 bar experiments which is consistent with the studies conducted by Uguna et al., (2012a & b). Higher gas yields were always generated from the experiments in the presence of montmorillonite clay, under both anhydrous (136 mg/g TOC) and 450 bar (116 mg/g TOC) compared to experiments without montmorillonite under the same experimental conditions. This is consistent with the previous studies where gas generation was significantly enhanced in the presence of clay minerals, especially montmorillonite (Tannenbaum and Kaplan, 1985; Tannenbaum et al., 1986; Huizinga et al., 1987a & b). In addition, higher gas yields were generated from the anhydrous compared to 450 bar experiments in the presence of montmorillonite compared to due to the presence of water diminishing the catalytic effects of clay minerals as suggested from previous studies (Tannenbaum and Kaplan, 1985; Tannenbaum et al., 1986; Huizinga et al., 1987a & b).

The alkene/alkane ratios for both bitumens also decrease with increasing water pressure at 350 °C for 24 h (Table 4.15c). When pressure was increased from 180 to 500 bar, the 14 % TOC bitumen shows a decrease in ethene/ethane and propene/propane ratio by a magnitude of 4 and 3, respectively. The 25 % TOC bitumen follows the same trend going from 180 to 500 bar, where the ethene/ethane and propene/propane ratio is reduced by of a magnitude of 2 and 4, respectively. At 900 bar and 350 °C for the 25 % TOC bitumen, the ethene/ethane ratio is reduced to 0, whereas the propene/propane ratio is decreased by a magnitude of 1.4 compared to 500 bar and 350 °C for 24 h (Table 4.15c). The decrease in gas yields observed with increase in pressure is consistent with previous studies where water pressure has been found to retard gas generation (Carr et al., 2009; Uguna et al., 2012a & b). The gas dryness ratios at 420 °C shows that in the presence of the montmorillonite, dryer gases were generated under both anhydrous (0.42) and high water pressure (0.48) conditions compared to the same experiments without the clay minerals (0.29 and 0.36 under anhydrous and 450 bar, respectively) due to the presence of minerals inducing more methane gas to be generated in relation to other hydrocarbon gases.

Table 4.15a. Individual and total gas (mg/g TOC of starting rock), gas dryness ratio ($C_1/(C_1\text{-}C_4)$), and alkene/alkane (C_2H_4/C_2H_6; C_3H_6/C_3H_8) from duplicate experiments (1 and 2) for the bitumen pyrolysed individually in the absence and presence of montmorillonite at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	$\frac{C_2H_4}{C_2H_6}$	$\frac{C_3H_6}{C_3H_8}$
Low pressure 1	180	350	2.75	0.11	2.62	0.24	2.11	1.04	8.9	0.31	0.042	0.114
Low pressure 2	180	350	2.97	0.09	2.71	0.31	2.06	1.09	9.2	0.32	0.033	0.150
High pressure 1	500	350	1.63	0.01	1.04	0.03	0.74	0.25	3.7	0.44	0.010	0.041
High pressure 2	500	350	1.52	0.01	0.96	0.02	0.65	0.19	3.4	0.45	0.010	0.031
Anhydrous (with montmorillonite)	25	420	57.9	0.22	29.9	0.80	33.6	13.9	136	0.42	0.007	0.024
Anhydrous	25	420	18.9	0.25	18.3	1.70	17.6	8.17	65	0.29	0.014	0.097
Low pressure 1	310	420	29.9	0.14	25.9	0.65	23.2	9.92	90	0.33	0.005	0.028
Low pressure 2	310	420	30.2	0.11	25.3	0.61	24.1	9.86	90	0.34	0.004	0.025
High pressure (with montmorillonite)	450	420	55.1	0.09	23.5	0.45	24.4	12.2	116	0.48	0.004	0.018
High pressure 1	450	420	31.3	0.08	24.0	0.36	21.9	9.04	87	0.36	0.003	0.016
High pressure 2	450	420	32.0	0.07	23.9	0.40	22.3	9.00	88	0.36	0.003	0.018

[1 & 2] duplicate runs

Table 4.15b. Individual and total gas (mg/g TOC of starting rock), gas dryness ratio ($C_1/(C_1\text{-}C_4)$), and alkene/alkane (C_2H_4/C_2H_6; C_3H_6/C_3H_8) from duplicate experiments (1 and 2) for the bitumen pyrolysed individually at 350 and 420 °C for 24 h (25 % TOC set).

. Experiment	Pressure (bar)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	$\frac{C_2H_4}{C_2H_6}$	$\frac{C_3H_6}{C_3H_8}$
Low pressure 1	180	350	3.30	0.06	3.01	0.20	2.17	1.08	10	0.34	0.020	0.092
Low pressure 2	180	350	3.29	0.06	2.98	0.21	2.16	1.01	10	0.34	0.020	0.097
High pressure	500	350	2.01	0.01	1.14	0.02	0.81	0.34	4.33	0.46	0.009	0.025
High pressure	900	350	1.01	0.00	0.76	0.01	0.57	0.25	2.59	0.39	0.000	0.018
Low pressure 1	310	420	37.2	0.12	29.5	0.58	26.1	13.6	107	0.35	0.004	0.022
Low pressure 2	310	420	37.2	0.11	29.5	0.56	26.1	13.6	107	0.35	0.004	0.021
High pressure	500	420	39.5	0.02	24.8	0.12	22.5	9.81	97	0.41	0.001	0.005
High pressure	900	420	51.2	0.01	29.3	0.05	27.7	11.1	119	0.43	0.000	0.002

[1 & 2] duplicate runs

Table 4.15c. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the bitumen pyrolysed individually at 350 °C for 24 h in Table 4.15a and b (14 and 25 % TOC set).

. Experiment	Pressure (bar)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	$\frac{C_2H_4}{C_2H_6}$	$\frac{C_3H_6}{C_3H_8}$
Low pressure												
14 % TOC set	180	350	2.86	0.10	2.67	0.28	2.09	1.07	9	0.32	0.037	0.134
25 % TOC set	180	350	3.30	0.06	3.00	0.21	2.17	1.05	10	0.34	0.020	0.097
High pressure												
14 % TOC set	500	350	1.58	0.01	1.00	0.03	0.70	0.22	3.6	0.45	0.010	0.043
25 % TOC set	500	350	2.01	0.01	1.14	0.02	0.81	0.34	4.33	0.46	0.009	0.025
25 % TOC set	900	350	1.01	0.00	0.76	0.01	0.57	0.25	2.59	0.39	0.000	0.018

Table 4.15d. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the bitumen pyrolysed individually at 420 °C for 24 h in Table 4.15a and b (14 and 25 % TOC set).

. Experiment	Pressure (bar)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	$\frac{C_2H_4}{C_2H_6}$	$\frac{C_3H_6}{C_3H_8}$
Anhydrous												
14 % TOC set (with montmorillonite)	25	420	57.9	0.22	29.9	0.80	33.6	13.9	136	0.42	0.007	0.024
14 % TOC set	25	420	18.9	0.25	18.3	1.70	17.6	8.17	65	0.29	0.014	0.097
Low pressure												
14 % TOC set	310	420	30.1	0.13	25.6	0.63	23.7	9.9	90	0.34	0.005	0.027
25 % TOC set	310	420	37.2	0.12	29.5	0.57	26.1	14	107	0.35	0.004	0.022
High pressure												
14 % TOC set (with montmorillonite)	450	420	55.1	0.09	23.5	0.45	24.4	12.2	116	0.48	0.004	0.018
14 % TOC set	450	420	31.7	0.08	24.0	0.38	22.1	9.0	88	0.36	0.003	0.017
25 % TOC set	500	420	39.5	0.02	24.8	0.12	22.5	9.81	97	0.41	0.001	0.005
25 % TOC set	900	420	51.2	0.01	29.3	0.05	27.7	11.1	119	0.43	0.000	0.002

4.4.2. Bitumen plus oil, liquid hydrocarbon and coke yields, and maturity assessment of aliphatic fractions of bitumen plus oil.

Table 4.16a lists the bitumen plus oil, aliphatic, aromatic, and total liquid hydrocarbon (aliphatic plus aromatic), and coke yields (mg/g TOC) generated from the 14 % TOC bitumen cracking experiments at 350 and 420 °C for 24 h, whereas Table 4.16b shows the bitumen plus oil yields and coke yields at 350 and 420°C for 24 h from the 25 % TOC bitumen cracking experiments. Table 4.16c & d list the mean of duplicate results for both bitumens at 350 and 420 °C, respectively.

At 350 °C for 24 h (Table 4.16c), the bitumen plus oil yield from the 14 % TOC bitumen cracking experiments were lowest at 180 bar (621 mg/g TOC) and increased at 500 bar (636 mg/g TOC). The 25 % TOC bitumen also follows the same trend at 350 °C where the total bitumen plus oil yield remaining at 180, 500 and 900 bar is 792, 832 and 945 mg/g TOC, respectively. The overall increase in bitumen plus oil yield with increasing water pressure at 350 °C is due to the effect of pressure preserving the bitumen and resultant oil from cracking into gas, and is consistent with the lower gas yield obtained at 500 and 900 bar compared to 180 bar as shown previously in Table 4.15c. This result is also consistent with previous studies (Carr et al., 2009; Uguna et al., 2012a & b). When the temperature was increased to 420 °C, the severe cracking of the bitumen to oil and gas at this temperature leads to a reduction in overall bitumen plus oil yields, which is consistent with the increased gas yields and the presence of coke at 420 °C in comparison to the 350 °C experiments. The bitumen plus oil yield also increases with increasing water pressure at 420 °C, where the bitumen plus oil yield from the 14 % TOC bitumen showed an increase from 167 mg/g TOC at 310 bar to 197 mg/g TOC at 450 bar. Similarly, the bitumen plus oil yield from the 25 % TOC bitumen increases from 168 mg/g TOC at 310 bar, to 225 and 225 mg/g TOC at 500 and 900 bar, respectively. The increase in bitumen plus oil yield with the increase in water pressure at 420 °C is due to more bitumen plus oil obtained under supercritical water conditions (500 and 900 bar) due to the promotional effect of water compared to super heated steam conditions (310 bar).

The experiments conducted with montmorillonite clay always generate lower bitumen plus oil yields under anhydrous (12 mg/g TOC) and 450 bar (111 mg/g TOC), compared to the same experiments without montmorillonite. This is due to the strong adsorption of the bitumen towards the clay mineral resulting in the lower bitumen plus oil yields as described by previous studies (Tannenbaum and Kaplan, 1985; Tannenbaum et al., 1986; Huizinga et al., 1987a &b). In the case of the liquid hydrocarbons (aliphatic and aromatic) generated from the 14 % TOC bitumen, similar total liquid hydrocarbon yields were generated at 180 (122 mg/g TOC) and 500 bar (129 mg/g TOC) at 350 °C (Table 5.15c) and is consistent with the same amount of bitumen plus oil remaining for both experiments.

The coke yields generated from the 14 % TOC bitumen at 420 °C were slightly reduced at 310 bar (280 mg/g TOC) to 450 bar (265 mg/g TOC). This is consistent with the slightly higher bitumen plus oil yield generated at 450 bar (197 mg/g TOC) compared to 310 bar (167 mg/g TOC). However, the 25 % TOC bitumen shows an increase from 310 bar (403 mg/g TOC) to 500 bar (444 mg/g TOC), whereas the coke yields generated from 900 bar (469 mg/g TOC) were similar to 500 bar. The similar coke yields is consistent with the same amount of bitumen plus oil yields generated at generated at 500 and 900 bar. The coke yields generated from the anhydrous experiments from the 14 % TOC bitumen are significantly higher compared to experiments conducted with water (310 and 450 bar) due to the direct cracking of the bitumen to form pyrobitumen and hydrocarbon gas in the absence of water. This is consistent with studies by Lewan (1992) where bitumen degrades to form insoluble pyrobitumen are more enhanced under anhydrous conditions compared to hydrous conditions. Experiments conducted in the presence of montmorillonite with the 14 % TOC bitumen always generate higher coke yields under anhydrous (380 mg/g TOC) and 450 bar (280 mg/g TOC) compared to experiments conducted without montmorillonite due to the bitumen being strongly adsorbed to the montmorillonite and being cracked to coke.

The maturity of the bitumen plus oil samples were also assessed using biomarker ratios; Pr/nC_{17} and Ph/nC_{18} ratios, the C_{29} and C_{30} $\beta\alpha/\alpha\beta$ hopane ratios, and C_{31} and C_{32} $\alpha\beta S/(\alpha\beta S + \alpha\beta R)$ hopane ratios from the 14 % TOC bitumen plus oil samples at 350 °C for 24 h (Table 4.17). The lower Pr/nC_{17} ratio at 180 bar (1.68) compared to 500 bar (1.85) at 350 °C indicates a more mature bitumen plus oil were generated at 180 bar. However, the Ph/nC_{18}, C_{29} and C_{30} $\beta\alpha/\alpha\beta$ hopane ratios, and the C_{31} and C_{32} $\alpha\beta S/(\alpha\beta S + \alpha\beta R)$ hopane ratios all show similar maturities were achieved due to the same ratios obtained at 180 bar and 500 bar. Overall, only the Pr/nC_{17} biomarker shows that faster thermal cracking are occurring at low pressure (180 bar), whereas retardation was observed when pressure was increased to 500 bar. This is consistent with the slightly higher gas yields generated from 180 bar compared to 500 bar.

Table 4.16a. Bitumen plus oil, liquid hydrocarbon and coke yields (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the bitumen pyrolysed individually in the absence and presence of montmorillonite at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Bitumen plus oil	Liquid hydrocarbon			Coke
				Aliphatic	Aromatic	Ali + Aro	
Low pressure 1	180	350	628	56	64	120	
Low pressure 2	180	350	614	58	66	124	
High pressure 1	500	350	632	61	71	132	
High pressure 2	500	350	640	59	67	126	
Anhydrous (with montmorillonite)	25	420	12	Not determined			380
Anhydrous	25	420	75	Not determined			332
Low pressure 1	310	420	168	Not determined			277
Low pressure 2	310	420	165				282
High pressure (with montmorillonite)	450	420	111	Not determined			280
High pressure 1	450	420	203	Not determined			260
High pressure 2	450	420	190				269

[1 & 2] duplicate runs

Table 4.16b. Bitumen plus oil and coke yields (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the bitumen pyrolysed individually at 350 and 420 °C for 24 h (25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Bitumen plus oil	Coke
Low pressure 1	180	350	793	
Low pressure 2	180	350	791	
High pressure	500	350	823	
High pressure	900	350	945	
Low pressure 1	310	420	167	403
Low pressure 2	310	420	169	402
High pressure	500	420	225	444
High pressure	900	420	225	469

[1 & 2] duplicate runs

Table 4.16c. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the bitumen pyrolysed individually at 350 °C for 24 h in Table 4.16a and b (14 and 25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Bitumen plus oil	Liquid hydrocarbon		
				Aliphatic	Aromatic	Ali + Aro
Low pressure						
14 % TOC set	180	350	621	57	65	122
25 % TOC set	180	350	792		Not determined	
High pressure						
14 % TOC set	500	350	636	60	69	129
25 % TOC set	500	350	823		Not determined	
25 % TOC set	900	350	945		Not determined	

Table 4.16d. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the bitumen pyrolysed individually at 420 °C for 24 h in Table 4.16a and b (14 and 25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Bitumen plus oil	Coke
Anhydrous				
14 % TOC set (with montmorillonite)	25	420	12	380
14 % TOC set	25	420	75	332
Low pressure				
14 % TOC set	310	420	167	280
25 % TOC set	310	420	168	403
High pressure				
14 % TOC set (with montmorillonite)	450	420	111	280
14 % TOC set	450	420	197	265
25 % TOC set	500	420	225	444
25 % TOC set	900	420	225	469

Table 4.17. Biomarker ratios [Pr/nC_{17} and Ph/nC_{18} ratios, C_{29} and C_{30} $\beta\alpha/\alpha\beta$ hopane ratios, and C_{31} to C_{32} $\alpha\beta$ S/($\alpha\beta$S + $\alpha\beta$R) hopane ratios] for the 14 % TOC bitumen pyrolysed individually at 350 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Isoprenoids		Hopanes			
			Pr/nC_{17}	Ph/nC_{18}	C_{29} $\beta\alpha/\alpha\beta$	C_{30} $\beta\alpha/\alpha\beta$	C_{31} S/(S+R)	C_{32} S/(S+R)
Low Pressure								
14 % TOC set	180	350	1.68	1.72	0.43	0.46	0.47	0.42
High pressure								
14 % TOC set	500	350	1.85	1.77	0.45	0.49	0.48	0.44

4.4.3. Carbon mass balances.

Table 4.18a & b. lists the carbon mass balances from the 14 and 25 % TOC bitumen cracking experiments, respectively. The carbon recoveries were slightly higher from the 25 % TOC bitumen cracking experiments at both 350 and 420 °C compared to the 14 % TOC bitumen. As water pressure increases, the carbon recovery was significantly increased to 99 %. As expected, lower carbon recoveries were obtained at 420 °C due to the loss of light fractions in the liquid product. The anhydrous experiments at 420 °C shows higher recoveries were achieved from experiments in the presence of the montmorillonite catalyst (79 %) compared to bitumen pyrolysed individually (70 %). Similarly, under high water pressure conditions (450 bar), higher recoveries were also attained for bitumen pyrolysed in the presence of montmorillonite (74 %) yields compared to the isolated bitumen experiments at 450 bar (78 %).

Table 4.18a. Carbon mass balance from duplicate experiments (1 and 2) for the bitumen pyrolysed individually in the absence and presence of montmorillonite at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Coke	Total recovered	% recovered
Low pressure 1	180	350	7.0	502	-	509	80
Low pressure 2	180	350	6.9	491	-	499	78
High pressure 1	500	350	2.9	506	-	509	80
High pressure 2	500	350	2.6	512	-	515	80
Anhydrous (with montmorillonite)	25	420	107	10	380	497	79
Anhydrous	25	420	52	60	332	444	70
Low pressure 1	310	420	71	134	277	482	76
Low pressure 2	310	420	71	132	282	485	76
High pressure (with montmorillonite)	450	420	90	89	280	459	74
High pressure 1	450	420	68	167	250	485	77
High pressure 2	450	420	69	152	269	490	76

[1 & 2] duplicate runs

Table 4.18b. Carbon mass balance from duplicate experiments (1 and 2) for the bitumen pyrolysed individually at 350 and 420 °C for 24 h (25 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Coke	Total recovered	% recovered
Low pressure 1	180	350	8	634	-	642	83
Low pressure 2	180	350	8	633	-	641	84
High pressure	500	350	3	658	-	662	87
High pressure	900	350	2	756	-	758	99
Low pressure 1	310	420	85	134	403	621	81
Low pressure 2	310	420	85	135	402	622	82
High pressure	500	420	76	180	444	700	92
High pressure	900	420	94	180	469	743	97

[1 & 2] duplicate runs

4.4.4. Main trends on isolated bitumen cracking experiments.

- Similar to previous experiments conducted on whole rock and partially matured source rock, the gas yield trends at 350 °C show pressure retardation effects on gas generation with increasing water pressure, whereas at 420 °C gas generation was not retarded with increasing water pressure.

- The bitumen plus oil yields at both 350 and 420 °C also increase with increasing water pressure. Liquid hydrocarbon yields generated from the 14 % TOC bitumen at 350 °C shows similar yields with increasing water pressure, whereas the biomarker ratios indicate slightly matured bitumen plus oil was obtained from 180 bar compared to 500 bar.

- The coke yields generated at 420 °C from the 14 % TOC bitumen decreases with increasing water pressure due to water pressure retarding coke formation from bitumen cracking. However, in the case of the 25 % TOC bitumen, a slight increase in coke yield was observed with increasing water pressure from 310 to 900 bar.

- In the presence of the montmorillonite clay under both hydrous and anhydrous experimental conditions, higher gas yields, dryer gases, low bitumen plus oil yields and higher coke yields were generated compared to the experiments conducted without montmorillonite due to the catalytic effects of the clay mineral. However, the catalytic effects were diminished under hydrous conditions.

4.5. Mixtures of isolated partially matured rock and bitumen experiment (Recombined mixture).

4.5.1. Gas yield.

The individual and total C_1-C_4 gas (mg/g TOC of starting rock), gas dryness ratio (C_1/(C_1-C_4)), and alkene/alkane ratios generated from recombined mixture experiments at 350 and 420 °C for 24 h are listed in Table 4.19a, whereas the mean of the duplicate results in Table 4.19a are listed in Table 4.19b. At 350 °C (Table 4.19b), the gas yields generated from 500 bar (7 mg/g TOC) were lower in comparison to 180 bar (13 mg/g TOC) due to water pressure retarding gas generation. With increasing pressure going from 180 to 500 bar at 350 °C, the ethene/ethane and propene/propane ratios were reduced by a factor of 2 and 9, respectively. At 420 °C, the gas yields generated were similar at 310 bar (149 mg/g TOC) and 450 bar (162 mg/g TOC), which is similar to what was observed previously from the 14 % TOC whole rock experiments (Table 4.1a). At 350 °C, dryer gases were also generated at 500 bar in comparison to the 180 bar experiments, whereas at 420 °C, the gas dryness were similar at 310 (0.39) and 450 bar (0.36). Overall, the gas yield trends for the recombined mixture experiments also follows the same trend as the whole rock experiments, where pressure retardation effects on gas generation were observed at 500 bar and 350 °C, whereas at 420 °C, water pressure was insufficient to retard gas generation.

Total 4.19a. Individual and total gas (mg/g TOC of starting rock), gas dryness ratio ($C_1/(C_1\text{-}C_4)$), and alkene/alkane (C_2H_4/C_2H_6; C_3H_6/C_3H_8) from duplicate experiments (1 and 2) for the mixtures of isolated partially matured source rock and bitumen at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$	$\frac{C_2H_4}{C_2H_6}$	$\frac{C_3H_6}{C_3H_8}$
Low pressure 1	180	24	350	4.14	0.08	3.95	0.28	3.07	1.41	13	0.32	0.020	0.091
Low pressure 2	180	24	350	4.02	0.07	3.93	0.23	3.10	1.41	13	0.32	0.018	0.074
High pressure 1	500	24	350	3.11	0.01	1.95	0.04	1.51	0.77	7.4	0.42	0.005	0.026
High pressure 2	500	24	350	2.53	0.01	1.89	0.02	1.44	0.71	6.6	0.38	0.005	0.014
Low pressure 1	310	24	420	57.4	0.05	37.3	0.26	35.7	16.3	147	0.39	0.001	0.007
Low pressure 2	310	24	420	58.4	0.04	36.6	0.25	37.5	17.1	150	0.39	0.001	0.007
High pressure 1	450	24	420	57.8	0.05	43.0	0.28	41.9	18.3	161	0.36	0.001	0.007
High pressure 2	450	24	420	58.1	0.04	43.0	0.25	42.6	18.9	163	0.36	0.001	0.006

[1 & 2] duplicate runs

Total 4.19b. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the mixtures of isolated partially matured source rock and bitumen in Table 4.19a and b (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)
Low pressure	180	24	350	4.08	0.08	3.94	0.26	3.09	1.41	13
High pressure	500	24	350	2.82	0.01	1.92	0.03	1.48	0.74	7
Low pressure	310	24	420	57.9	0.05	37.0	0.26	36.6	16.7	149
High pressure	450	24	420	58.0	0.05	43.0	0.27	42.3	18.6	162

[1 & 2] duplicate runs

4.5.2. Bitumen plus oil and liquid hydrocarbon yields, and maturity assessment of aliphatic fractions of bitumen plus oil.

Table 4.20a lists the bitumen plus oil yield, aliphatic, aromatic, and total liquid hydrocarbon (aliphatic plus aromatic) yields (mg/g TOC of starting rock) generated from the recombine mixture experiments, whereas the mean value of duplicate results are listed in Table 4.20b. At 350 °C, bitumen plus oil yields was similar at 180 bar (464 mg/g TOC) and 500 bar (438 mg/g TOC). This is consistent with liquid hydrocarbon yields, where the aliphatic and aromatic yields are also the same at both low and high pressure at 350 °C. The amount of aliphatics at 180 and 500 bar were 50 and 52 mg/g TOC, respectively, whereas the aromatics yields at 180 and 500 bar were 84 and 85 mg/g initial TOC, respectively). At 420 °C, the bitumen plus oil yield was doubled at 450 bar (136 mg/g TOC) in comparison to 310 bar (73 mg/g TOC), which is consistent to what was observed from the 14 % TOC whole rock experiments.

Table 4.20a. Bitumen plus oil and liquid hydrocarbon yields (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the mixtures of isolated partially matured source rock and bitumen experiments at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp(°C)	Bitumen plus oil	Liquid hydrocarbon		
				Aliphatic	Aromatic	Ali + Aro
Low pressure 1	180	350	462	49	85	134
Low pressure 2	180	350	466	51	86	137
High pressure 1	500	350	435	52	83	135
High pressure 2	500	350	441	52	86	138
Low pressure 1	310	420	71	Not determined		
Low pressure 2	310	420	75			
High pressure 1	450	420	140	Not determined		
High pressure 2	450	420	132			

[1 & 2] duplicate runs

Table 4.20b. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the mixtures of isolated partially matured source rock and bitumen in Table 4.20a (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Bitumen plus oil	Liquid hydrocarbon		
				Aliphatic	Aromatic	Ali + Aro
Low pressure	180	350	464	50	86	136
High pressure	500	350	438	52	85	137
Low pressure	310	420	73	Not determined		
High pressure	450	420	136	Not determined		

Table 4.21 list the biomarker ratios from the mixtures of isolated partially matured source rock and bitumen experiments at 350 °C for 24 h. Some of the biomarkers were not determined due to the high level of noise in the peaks. However, the determined Pr/nC_{17} ratios, C_{29} $\beta\alpha/\alpha\beta$ and the C_{31} $\alpha\beta S/(\alpha\beta S + \alpha\beta R)$ hopane ratios show similar maturities were obtained from the bitumen plus oil obtained at 180 bar compared to 500 bar.

Table 4.21. Biomarker [Pr/nC_{17} and Ph/nC_{18} ratios, C_{29} and C_{30} $\beta\alpha/\alpha\beta$ hopane ratios, and C_{31} to C_{32} $\alpha\beta S/(\alpha\beta S + \alpha\beta R)$ hopane ratios] for the mixtures of isolated partially matured source rock and bitumen experiments at 350 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Isoprenoids		Hopanes			
			Pr/nC_{17}	Ph/nC_{18}	C_{29} $\beta\alpha/\alpha\beta$	C_{30} $\beta\alpha/\alpha\beta$	C_{31} S/(S+R)	C_{32} S/(S+R)
Mixture	180	350	1.59	1.53	0.11	0.19	0.60	N.D
Mixture	500	350	1.60	ND	0.12	N.D	0.58	0.57

ND: Not determined

4.5.3. Residual TOC and carbon mass balances.

Table 4.22a lists the residual rock mass (g) and residual rock TOC (%) from the 14 % TOC recombine mixture experiment at 350 and 420 °C for 24 h, whereas the Table 4.21b lists the duplicate results in Table 4.22a. At 350 °C, similar residual TOC was generated at 180 bar (6.3 % TOC) and 500 bar (6.6 % TOC) which is consistent with the same amount of bitumen plus oil yield remaining at 180 and 500 bar (Table 4.20b). At 420 °C, the residual TOC was slightly reduced from 9.0 % TOC at 310 bar to 8.3 % TOC at 450 bar, and follows the same trend as the whole rock experiments. The residual TOC are always higher from the mixtures of isolated partially matured rock and bitumen experiments compared to the whole rock experiments. This is due to the strong retention of the bitumen towards the partially matured source rock, where the bitumen retained is cracked to form pyrobitumen and increases the residual TOC for the recombined mixtures. The carbon mass balances from the mixtures of isolated partially matured rock bitumen experiments that are listed in Table 4.23, shows similar recoveries were generated under all experimental conditions, ranging between 74 to 80 %.

Table 4.22a. Residual rock mass (g) and residual rock TOC (%) from duplicate experiments (1 and 2) for the mixtures of isolated partially matured source rock and bitumen experiments at 350 and 420 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Residual rock (g)	Residual rock TOC (%)
Low pressure 1	180	24	350	5.8	6.3
Low pressure 2	180	24	350	5.8	6.3
High pressure 1	500	24	350	5.7	6.6
High pressure 2	500	24	350	5.7	6.6
Low pressure 1	310	24	420	5.6	9.0
Low pressure 2	310	24	420	5.6	9.1
High pressure 1	450	24	420	5.8	8.4
High pressure 2	450	24	420	5.8	8.3

[1 & 2] duplicate runs

Table 4.22b. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the mixtures of isolated partially matured source rock and bitumen in Table 4.22a (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Residual rock (g)	Residual rock TOC (%)
Low pressure	180	24	350	5.8	6.3
High pressure	500	24	350	5.7	6.6
Low pressure	310	24	420	5.6	9.0
High pressure	450	24	420	5.8	8.3

Table 4.23. Carbon mass balance from duplicate experiments (1 and 2) for the mixtures of isolated partially matured source rock and bitumen at 350 and 420 °C for 24 h (14 % TOC set).

Experiments	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual Rock	Total recovered	% recovered
Low pressure 1	180	24	350	10	370	381	761	80
Low pressure 2	180	24	350	10	373	392	775	80
High pressure 1	500	24	350	6	348	347	701	78
High pressure 2	500	24	350	5	353	349	707	76
Low pressure 1	310	24	420	116	57	506	678	73
Low pressure 2	310	24	420	118	60	510	688	74
High pressure 1	450	24	420	127	112	484	724	76
High pressure 2	450	24	420	129	106	476	710	77

[1 & 2] duplicate runs

4.5.4. Main Trends on mixtures of partially matured source rock and bitumen pyrolysis experiments.

- Similar gas yield and bitumen plus oil yield trends were observed from the recombined mixture experiments compared to the whole rock experiments, indicating that that the recombined mixture are comparable to the whole rock experiments.

- Similar liquid hydrocarbon yields and similar biomarker ratio maturities were generated under low (180 bar) and high water pressure (500 bar) experiments at 350 °C.

- The residual TOCs are relatively higher from the mixtures of isolated partially matured rock and bitumen experiments compared to the whole rock experiments due to extensively adsorbed bitumen increasing the residual TOC in the form of coke. However, there are no significant pressure effects observed on the pyrobitumen formation as similar residual TOCs were obtained from high and low pressure experiments at 350 °C, and from high and low pressure experiments at 420 °C.

4.6. Control experiment.

In order to ensure that the whole rock pyrolysis experiments (Section 4.1) will be comparable to the other experiments where the bitumen was first generated before the partially matured source rock and generated bitumen were further pyrolysed (Section 4.2 to 4.5, and the combined results in Chapter 5), a control experiment was performed. After the bitumen generation experiment, the gas was collected and analysed, before the whole rock containing the bitumen was further pyrolysed at 350 °C for 24 h, without separating the bitumen generated.

The individual and total C_1-C_4 gas (mg/g TOC of starting rock) and gas dryness ratio ($C_1/(C_1$-$C_4)$), from the control experiments at 180 bar and 350 °C for 24 h are listed in Table 4.24a, whereas Table 4.24b list the mean results in Table 4.24a. Table 4.25a lists the bitumen plus oil yield (mg/g TOC), residual rock weight (g) and residual TOC (%), from the control experiments, whereas Table 4.25b lists the mean values of duplicate experiments in Table 4.25a. The mean liquid hydrocarbon yield generated from the duplicate control experiments are listed in Table 4.26. The carbon mass balances from the control experiments are shown in Table 4.27.

- The overall gas yields generated from the control experiment (23 mg/g TOC) were similar to the total gas yields obtained from the whole experiments (21 mg/g TOC) under the same experimental conditions at 180 bar and 350 °C (Table 4.24b).

- The bitumen plus oil yield and liquid hydrocarbon yield was lower from the control experiments compared to the whole rock experiments, which is consistent with the higher residual TOC obtained from the control experiments (Table 4.25b). The higher residual TOC is due to longer residence time inducing more pyrobitumen to be formed from the control experiments (31 h) compared to the whole rock experiment (24 h).

- Due to the minor differences between the hydrocarbon yields from the control experiments and the whole rock experiments, the results indicate that the experiment in Section 4.2 to 4.5 are comparable to the whole rock experiments (Section 4.1). In addition, the recoveries from the control and whole rock experiments are similar (Table 4.27).

Table 4.24a. Individual and total gas (mg/g TOC of starting rock) and gas dryness ratio ($C_1/(C_1\text{-}C_4)$) ratio from duplicate experiments (1 and 2) for the control experiments at low pressure (180 bar) at 350 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)	$\frac{C_1}{(C_1\text{-}C_4)}$
Low pressure											
Bitumen generation 1	160	7	340	2.12	0.08	1.60	0.20	1.31	0.55	5.9	0.36
Bitumen generation 2	160	7	340	2.17	0.09	1.62	0.18	1.37	0.54	6.0	0.36
Control 1a	180	24	350	5.12	0.07	5.12	0.29	4.02	1.84	16	0.31
Control 2a	180	24	350	5.21	0.08	5.14	0.34	3.99	1.89	17	0.31
Overall gas yield 1b (mg/g TOC of starting rock)				7.24	0.15	6.72	0.49	5.33	2.39	22	
Overall gas yield 2b (mg/g TOC of starting rock)				7.38	0.17	6.76	0.52	5.36	2.43	23	
14 % TOC Whole rock (mg/g TOC of starting rock)	180	24	350	6.70	0.10	6.41	0.42	5.13	1.95	21	0.32

[1 & 2] duplicate runs, [a] partially matured source rock and bitumen generated from bitumen generation experiments without separating the bitumen. [b] sum of gas yields from bitumen generation and control experiments.

Table 4.24b. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the control experiments in Table 4.24a (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	CH_4	C_2H_6	C_3H_8	C_4H_{10}	Total (C_1-C_4)
Low pressure								
Bitumen generation	160	7	340	2.15	1.61	1.34	0.55	5.95
Control a	180	24	350	5.17	5.13	4.01	1.87	17
Overall gas yield b (mg/g TOC of starting rock)				7.31	6.74	5.35	2.41	23
14 % TOC Whole rock (mg/g TOC of starting rock)	180	24	350	6.70	6.41	5.13	1.95	21

[a] partially matured source rock and bitumen generated from bitumen generation experiments without separating the bitumen.

[b] sum of gas yields from bitumen generation and control experiments.

Table 4.25a. Bitumen plus oil yield (mg/g TOC of starting rock), residual rock mass (g) and residual rock TOC (%) from duplicate experiments (1 and 2) for the control experiments at low pressure (180 bar) at 350 °C for 24 h (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Bitumen plus oil	Residual rock (g)	Residual rock TOC (%)
Low pressure						
Bitumen generation 1	160	7	340	-	-	-
Bitumen generation 2	160	7	340	-	-	-
Control 1a	180	24	350	473	6.0	6.3
Control 2a	180	24	350	467	6.0	6.3
Overall yield 1 (mg/g initial TOC)				473	6.0	6.3
Overall yield 2 (mg/g initial TOC)				467	6.0	6.3
14 % TOC Whole rock	180	24	350	563	6.0	5.0

[1 & 2] duplicate runs

[a] partially matured source rock and bitumen generated from bitumen generation experiments without separating the bitumen.

Table 4.25b. Mean values (mg/g TOC of starting rock) from duplicate experiments (1 and 2) for the control experiments in Table 4.25a (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Bitumen plus oil	Residual rock (g)	Residual rock TOC (%)
Low pressure						
Control a	180	24	350	470	5.9	6.3
14 % TOC Whole rock	180	24	350	563	5.9	5.0

[a] partially matured source rock and bitumen generated from bitumen generation experiments without separating the bitumen.

Table 4.26. Liquid hydrocarbon yields (mg/g TOC of starting rock), including mean values from duplicate experiments (1 and 2) for the control experiments at low pressure (180 bar) at 350 °C for 24 h (14 % TOC set)

Experiment	Pressure (bar)	Temp (°C)	Liquid hydrocarbon		
			Aliphatic	Aromatic	Ali + Aro
Control 1a	180	350	62	92	154
Control 2a	180	350	65	98	163
Control (mean)	180	350	64	95	159
14 % TOC Whole rock	180	350	79	107	186

[1 & 2] duplicate runs

[a] partially matured source rock and bitumen generated from bitumen generation experiments without separating the bitumen.

Table 4.27. Carbon mass balance from duplicate experiments (1 and 2) for the control experiments at low pressure (180 bar) at 350 °C for 24 h (14 % TOC set)

Experiment	Pressure (bar)	Temp (°C)	Total (C_1-C_4)	Bitumen	Residual rock	Total recovered	% recovered
Control 1a	180	350	18	379	373	769	77
Control 2a	180	350	18	374	370	762	76
14 % TOC Whole rock	180	350	16	450	295	762	77

[1 & 2] duplicate runs

[a] partially matured source rock and bitumen generated from bitumen generation experiments without separating the bitumen.

Chapter 5: Comparison of yields for whole rock against those from the isolated fractions and recombined mixture.

This chapter compares results obtained from the whole rock experiments to those from the isolated fractions (partially matured source rock and bitumen cracking) and recombined mixtures. In the case of the whole rock experiments, the gas, liquid and solid product were all generated from the initial whole rock. For the isolated fraction experiments, the total gas yield is the summation of gases generated from the bitumen generation, isolated partially matured source rock and isolated bitumen cracking experiments. The bitumen plus oil yields from the isolated fraction experiments is a summation of the bitumen plus oil generated from the isolated partially matured source rock and isolated bitumen cracking experiments. The solid product generated from the isolated fraction experiments is from the residual rock (partially matured source rock) and coke (from isolated bitumen cracking experiments at 420 °C). In the case of the recombined mixtures, the gas yields were determined by summation of the gases generated from the bitumen generation and recombined mixture experiments. The bitumen plus oil yields and the solid products will be generated from the initial recombined mixtures. The coke yields in the residual source rocks were determined by a Thermo Electron FlashEX 1112 Elemental analyser. Tables 5.1 to 5.4 lists the product yields from the isolated fraction and recombined mixture experiments for the 14 % TOC source rocks, while Tables 5.5 to 5.6 lists the product yields from the isolated fraction experiments for the 25 % TOC source rocks.

Table 5.1a. Total gas, bitumen plus oil yields (mg/g TOC of starting rock), residual rock TOC (%), initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the isolated partially matured source rock and bitumen pyrolysed individually at low pressure (180 bar) at 350 °C (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
Bitumen generation[b] 1	160-1	7	340	6.0		5.8	
Bitumen generation[c] 2	160-2	7	340	5.3		5.8	
Partially matured source rock pyrolysis 1	180	24	350	3.0	42	3.9	302
Partially matured source rock pyrolysis 2	180	24	350	3.1	38	4.0	305
Bitumen pyrolysis 1	180	24	350	8.9	628		638
Bitumen pyrolysis 2	180	24	350	9.2	614		640
Overall yield (mg/g TOC of starting rock) 1				18	670	3.9	
Overall yield (mg/g TOC of starting rock) 2				18	652	4.0	
Whole rock (mg/g TOC of starting rock)	180	24	350	21	563	5.0	1000
Control (mg/g TOC of starting rock)	180	24	350	23	470	6.3	1000

[b and c] Bitumen from experiment 1 and 2, respectively (Table 4.9a).

Table 5.1b. Total gas, bitumen plus oil yields (mg/g TOC of starting rock), residual rock TOC (%), initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the isolated partially matured source rock and bitumen pyrolysed individually at high water pressure (500 bar) at 350 °C (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
Bitumen generation[b] 1	160-3	7	340	5.8		5.8	
Bitumen generation[c] 2	160-4	7	340	5.9		5.8	
Partially matured source rock pyrolysis 1	500	24	350	1.1	49	4.2	304
Partially matured source rock pyrolysis 2	500	24	350	1.2	54	4.3	303
Bitumen pyrolysis 1	500	24	350	3.7	632		632
Bitumen pyrolysis 2	500	24	350	3.4	640		642
Overall yield (mg/g TOC of starting rock) 1				11	681	4.2	
Overall yield (mg/g TOC of starting rock)) 2				10	694	4.3	
Whole rock (mg/g TOC of starting rock)	500	24	350	17	609	5.1	1000

[b and c] Bitumen from experiment 3 and 4, respectively (Table 4.9a).

Table 5.2a. Total gas, bitumen plus oil, coke yields (mg/g TOC of starting rock), residual rock TOC (%), initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the isolated partially matured source rock and bitumen pyrolysed individually at low pressure (310 bar) at 420 °C (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Coke	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
Bitumen generation[b] 1	160-5	7	340	5.8			5.2	
Bitumen generation[c] 2	160-6	7	340	5.8			5.2	
Partially matured source rock pyrolysis 1	310	24	420	23	12	251	4.5	299
Partially matured source rock pyrolysis 2	310	24	420	22	12	249	4.5	299
Bitumen pyrolysis 1	310	24	420	90	168	277		633
Bitumen pyrolysis 2	310	24	420	90	165	282		637
Overall yield (mg/g TOC of starting rock) 1				118	180	277	4.5	
Overall yield (mg/g TOC of starting rock) 2				118	177	282	4.5	
Whole rock (mg/g TOC of starting rock)	310	24	420	188	101	524	8.9	1000

[b and c] Bitumen from experiment 5 and 6, respectively (Table 4.9a).

Table 5.2b. Total gas, bitumen plus oil, coke yields (mg/g TOC of starting rock), residual rock TOC (%), initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the isolated partially matured source rock and bitumen pyrolysed individually at high water pressure (450 bar) at 420 °C (14 % TOC set).

Experiment		Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Coke	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
Bitumen generation[b]	1	160-7	7	340	6.2	779		5.2	
Bitumen generation[c]	2	160-8	7	340	5.9	805		5.2	
Partially matured source rock pyrolysis	1	450	24	420	23	28		4.7	304
Partially matured source rock pyrolysis	2	450	24	420	22	24		4.7	303
Bitumen pyrolysis	1	450	24	420	87	203	260		623
Bitumen pyrolysis	2	450	24	420	88	190	269		644
Overall yield (mg/g initial TOC)	1				116	231	260	4.7	
Overall yield (mg/g initial TOC)	2				116	214	269	4.7	
Whole rock (mg/g TOC of starting rock)		450	24	420	191	159	447	7.7	1000

[b and c] Bitumen from experiment 7 and 8, respectively (Table 4.9a).

Table 5.3a. Total gas, bitumen plus oil yields (mg/g TOC of starting rock), residual rock TOC (%), amount of initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the recombined mixtures pyrolysed at low pressure (180 bar) at 350 °C (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
Bitumen generation[b] 1	160-9	7	340	6.2	785	5.2	
Bitumen generation[c] 2	160-10	7	340	6.0	792	5.2	
Recombine mixture 1	180	24	350	13	462	6.3	304 & 628
Recombine mixture 2	180	24	350	13	466	6.3	303 & 634
Overall yield (mg/g initial TOC) 1				19	462	6.3	
Overall yield (mg/g initial TOC) 2				19	466	6.3	
Whole rock (mg/g TOC of starting rock)	180	24	350	21	563	5.0	1000

[b and c] Bitumen from experiment 9 and 10, respectively (Table 4.9a).

Table 5.3b. Total gas, bitumen plus oil yields (mg/g TOC of starting rock), residual rock TOC (%), amount of initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the recombined mixtures pyrolysed at high water pressure (500 bar) at 350 °C (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
Bitumen generation[b] 1	160-11	7	340	5.7	801	5.3	
Bitumen generation[c] 2	160-12	7	340	5.9	820	5.2	
Recombine mixture 1	500	24	350	7.4	435	6.6	297 & 641
Recombine mixture 2	500	24	350	6.6	441	6.6	303 & 656
Overall yield (mg/g initial TOC) 1				13	435	6.6	
Overall yield (mg/g initial TOC) 2				13	441	6.6	
Whole rock (mg/g TOC of starting rock)	500	24	350	17	609	5.1	1000

[b and c] Bitumen from experiment 11 and 12, respectively (Table 4.9a).

Table 5.4a. Total gas, bitumen plus oil yields (mg/g TOC of starting rock), residual rock TOC (%), amount of initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the recombined mixtures pyrolysed at low pressure (310 bar) at 420 °C (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
Bitumen generation[b] 1	160-13	7	340	6.2	789	5.2	
Bitumen generation[c] 2	160-14	7	340	5.7	787	5.2	
Recombine mixture 1	310	24	420	147	71	9.0	301 & 631
Recombine mixture 2	310	24	420	150	75	9.1	302 & 630
Overall yield (mg/g initial TOC) 1				153	71	9.0	
Overall yield (mg/g initial TOC) 2				156	75	9.1	
Whole rock (mg/g TOC of starting rock)	310	24	420	188	101	8.9	1000

[b and c] Bitumen from experiment 13 and 14, respectively (Table 4.9a).

Table 5.4b. Total gas, bitumen plus oil yields (mg/g TOC of starting rock), residual rock TOC (%), amount of initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the recombined mixtures pyrolysed at high water pressure (450 bar) at 420 °C (14 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
Bitumen generation[b] 1	160-15	7	340	5.9	805	5.2	
Bitumen generation[c] 2	160-16	7	340	6.0	782	5.2	
Recombine mixture 1	450	24	420	161	140	8.4	303 & 644
Recombine mixture 2	450	24	420	163	132	8.3	303 & 626
Overall yield (mg/g TOC of starting rock) 1				167	140	8.4	
Overall yield (mg/g TOC of starting rock) 2				169	132	8.3	
Whole rock (mg/g TOC of starting rock)	450	24	420	191	159	7.7	1000

[b and c] Bitumen from experiment 15 and 16, respectively (Table 4.9a).

Table 5.5a. Total gas, bitumen plus oil yields (mg/g TOC of starting rock), residual rock TOC (%), initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the isolated partially matured source rock and bitumen pyrolysed individually at low pressure (180 bar) at 350 °C (25 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
Bitumen generation[b] 1	180-1	6	350	16	962	6.2	
Bitumen generation[c] 2	180-2	6	350	16	954	6.2	
Partially matured source rock pyrolysis 1	180	24	350	1.0	14	4.5	155
Partially matured source rock pyrolysis 2	180	24	350	0.99	15	4.5	154
Bitumen pyrolysis 1	180	24	350	10	793		770
Bitumen pyrolysis 2	180	24	350	10	791		763
Overall yield (mg/g TOC of starting rock) 1				27	806	4.5	
Overall yield (mg/g TOC of starting rock) 2				26	810	4.5	
25 % TOC Whole rock (mg/g TOC of starting rock)	180	24	350	39	576	14.8	1000

[b and c] Bitumen from experiment 1 and 2, respectively (Table 4.9b).

Table 5.5b. Total gas, bitumen plus oil yields (mg/g TOC of starting rock), residual rock TOC (%), initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the isolated partially matured source rock and bitumen pyrolysed individually at high water pressure (500 and 900 bar) at 350 °C (25 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
Bitumen generation[b]	180-3	6	350	16	952	6.2	
Partially matured source rock pyrolysis	500	24	350	0.49	15	4.4	152
Bitumen pyrolysis	500	24	350	4.33	823		762
Overall gas yield (mg/g TOC of starting rock)				21	838	4.4	
25 % TOC Whole rock (mg/g TOC of starting rock)	500	24	350	21	643	11.8	1000
Bitumen generation[c]	180-4	6	350	16	957	6.0	
Partially matured source rock pyrolysis	900	24	350	0.35	13	5.7	148
Bitumen pyrolysis	900	24	350	2.59	945		766
Overall gas yield (mg/g TOC of starting rock)				18	958	5.7	
25 % TOC Whole rock (mg/g TOC of starting rock)	900	24	350	15	666	11.6	1000

[b and c] Bitumen from experiment 3 and 4, respectively (Table 4.9b).

Table 5.6a. Total gas, bitumen plus oil yields (mg/g TOC of starting rock), residual rock TOC (%), coke yields (mg/g TOC of starting rock) and initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the isolated partially matured source rock and bitumen pyrolysed individually at low pressure (310 bar) at 420 °C (25 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Coke	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
Bitumen generation[b]	180-5	6	350	16	953		6.2	
Bitumen generation[c]	180-6	6	350	16	941		6.2	
Partially matured source rock pyrolysis	310	24	420	9	30		4.4	153
Partially matured source rock pyrolysis[d]	310	24	420	9	32		4.3	153
Bitumen pyrolysis	310	24	420	107	168	422		762
Bitumen pyrolysis[d]	310	24	420	107	169	419		753
Overall yield (mg/g TOC of starting rock)				139	198	422	4.4	
Overall yield (mg/g TOC of starting rock)[d]				138	201	419	4.32	
25 % TOC Whole rock (mg/g TOC of starting rock)	310	24	420	223	151	415	14.4	1000

[b and c] Bitumen from experiment 5 and 6, respectively (Table 4.9b).

Table 5.6b. Total gas, bitumen plus oil yields (mg/g TOC of starting rock), residual rock TOC (%), coke yields (mg/g TOC of starting rock) and initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the isolated partially matured source rock and bitumen pyrolysed individually at high water pressure (500 and 900 bar) at 420 °C (25 % TOC set).

Experiment	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Coke	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
Bitumen generation[b]	180-7	6	420	16	954		6.2	
Partially matured source rock pyrolysis	500	24	420	7	11		4.7	152
Bitumen pyrolysis	500	24	420	97	225	444		763
Overall yield (mg/g TOC of starting rock)				120	235	444	4.7	
25 % TOC Whole rock (mg/g TOC of starting rock)	500	24	420	181	322	279	11.1	1000
Bitumen generation[c]	180-8	6	420	16	954		6.2	
Partially matured source rock pyrolysis	900	24	420	6	12		5.0	152
Bitumen pyrolysis	900	24	420	119	225	469		763
Overall yield (mg/g TOC of starting rock)				141	237	469	5.0	
25 % TOC Whole rock (mg/g TOC of starting rock)	900	24	420	189	338	275	11.1	1000

[b and c] Bitumen from experiment 7 and 8, respectively (Table 4.9b)

5.1. Gas yields.

Figures 5.1 to 5.6 and Tables 5.1 to 5.6 compares the total C_1-C_4 hydrocarbon gas yields for the pyrolysis experiments at 350 and 420 °C for 24 h at low and high pressure from the 14 and 25 % TOC set of whole rock, isolated partially matured source rock and bitumen (isolated fraction) and their recombined mixture experiments. In these plots, the gas yields contains 2 components (yields from partially matured source rock and bitumen cracking), with gas yields from bitumen generation not added as in those listed in Tables 5.1 to 5.6. For experiments with duplicate data set the mean value was used for all plots. The average amount of C_1-C_4 gas generated from multiple bitumen generation experiments is approx. 6 and 16 mg/g TOC from the 14 and 25 % TOC source rocks, respectively, and will be deducted from the C_1-C_4 gas yields generated from the whole rock experiments (Figs. 5.1. to 5.6). However, for the experiments at 500 bar (Fig. 5.2b) and 900 bar (Fig. 5.3) at 350 °C using the 25 % TOC whole rock, the amount of gas deducted in these plots were 5 mg/g TOC, which is the amount of gas generated from a 25 % TOC bitumen generation experiment at 500 bar in Uguna et al., (2012a).

At 350 °C for 24 h, gas yields generated from the isolated fractions (12 mg/g TOC), recombined mixtures (13 mg/g TOC), and whole rock experiments (15 mg/g TOC) were similar from the 14 % TOC source rocks at 180 bar (Fig. 5.1a). However, under the same conditions (180 bar at 350 °C), the 25 % TOC whole rock experiments (24 mg/g TOC) generated more than twice the amount of the isolated fractions experiments (11 mg/g TOC) as shown in Fig. 5.1b. At 350 °C and 500 bar (Fig. 5.2a) the gas yields from the 14 % TOC set of experiments generates 5, 7 and 11 mg/g TOC from the isolated fractions, recombined mixtures and whole rock experiments, respectively. The gas yields from the 25 % TOC whole rock experiment were 3 folds higher at both 500 bar (Fig. 5.2b) and 900 bar (Fig. 5.3) compared to the isolated fraction experiments under the same experimental conditions.

At 420 °C, the gas yields from the 14 % TOC source rocks at 310 bar from the isolated fraction, recombined mixtures and whole rock experiments were 113, 149 and 182 mg/g TOC, respectively (Fig. 5.4a), whereas in the case of the 25 % TOC source rocks at 310 bar (Fig. 5.4b), the whole rock experiments (207 mg/g TOC) generated 78 % more gas compared to the isolated fraction experiments (116 mg/g TOC). At 450 bar and 420 °C (Fig. 5.5a) the gas yields from the 14 % TOC source rocks generated 110, 162 and 185 mg/g TOC from the isolated fraction, recombined mixtures and whole rock experiments, respectively. Under high pressure conditions (500 and 900 bar) from the 25 % TOC source rocks, the gas yields from the whole rock experiments were approx. 1.7 and 1.5 folds higher compared to the isolated fraction experiments at 500 bar (Fig. 5.5b) and 900 bar (Fig. 5.6), respectively.

Overall, the higher gas yields generated from the whole rock experiments compared to recombined mixtures and isolated fraction experiments implies that the close interaction between kerogen/bitumen and mineral matter is important in facilitating hydrocarbon gas generation compared to when bitumen and partially matured source rocks are pyrolysed individually. The intermediate gas yields generated from the recombined mixtures is due to poorer interactions between kerogen/bitumen and mineral matter compared to whole rock experiments. Furthermore, Figures 5.1 to 5.6 shows that most of the hydrocarbon gases are contributed from bitumen cracking experiments, which is consistent with the studies by Erdmann and Horsfield (2006).

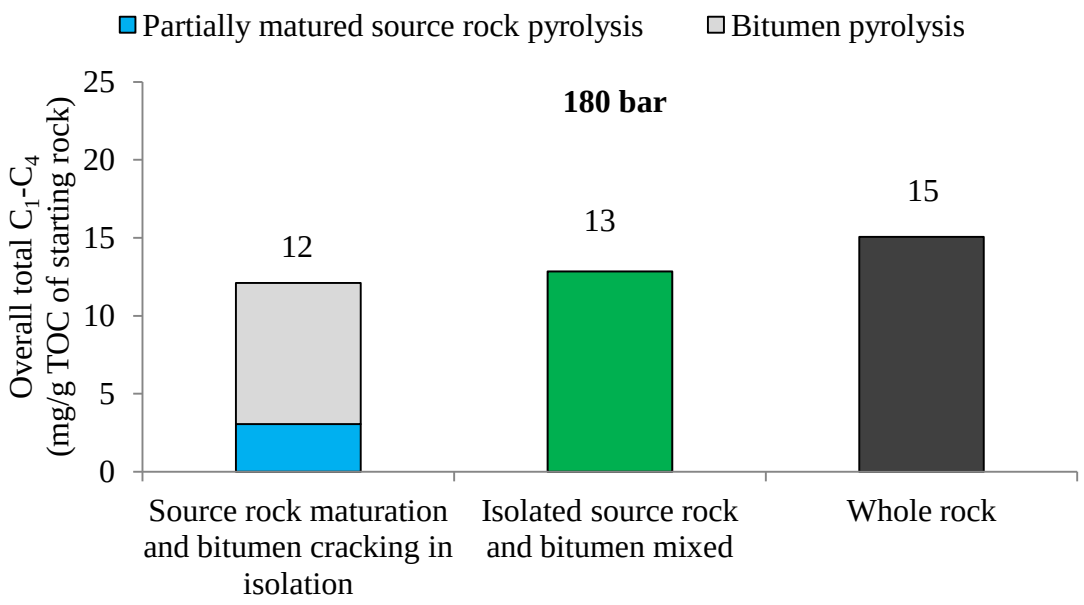

Fig. 5.1a. Total gas yields at 180 bar at 350 °C for 24 h (14 % TOC set).

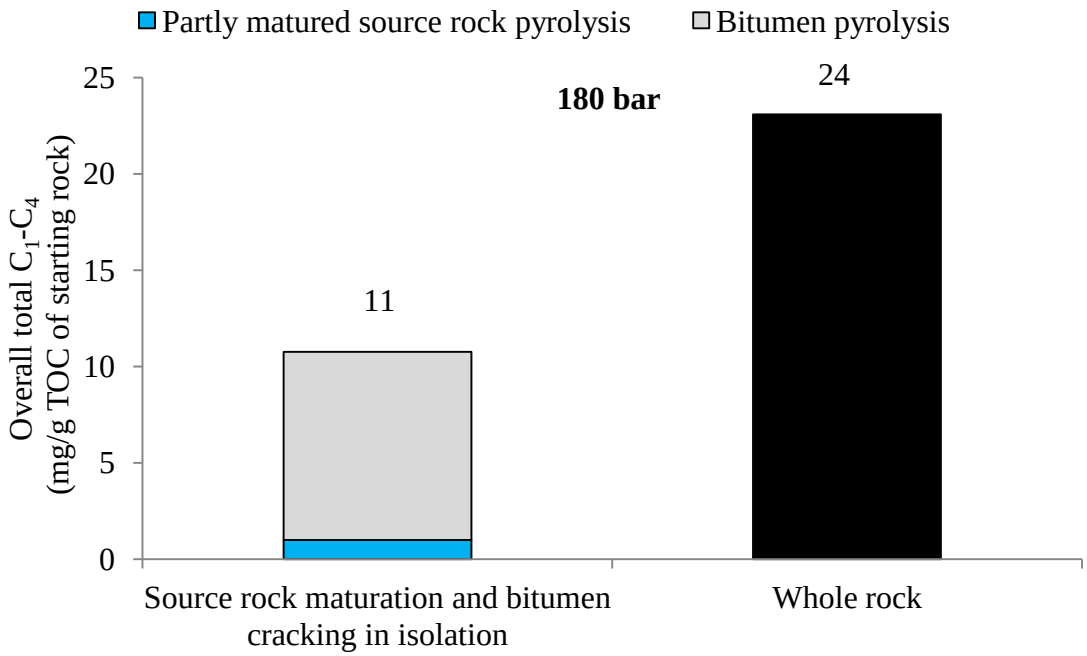

Fig. 5.1b. Total gas yields at 180 bar at 350 °C for 24 h (25 % TOC set).

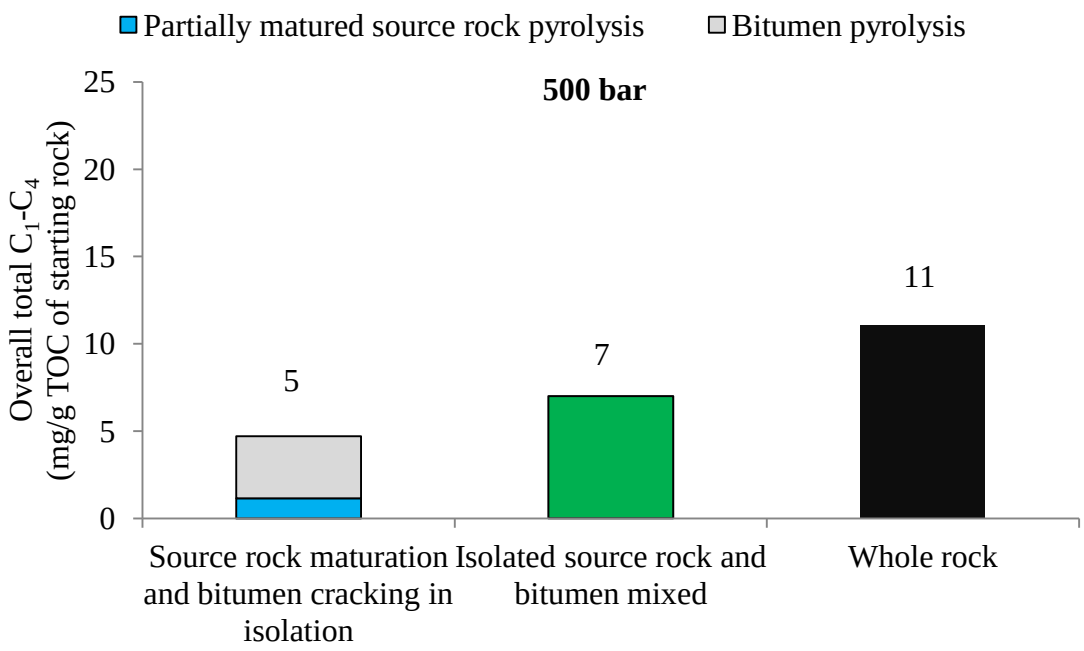

Fig. 5.2a. Total gas yields at 500 bar at 350 °C for 24 h (14 % TOC set).

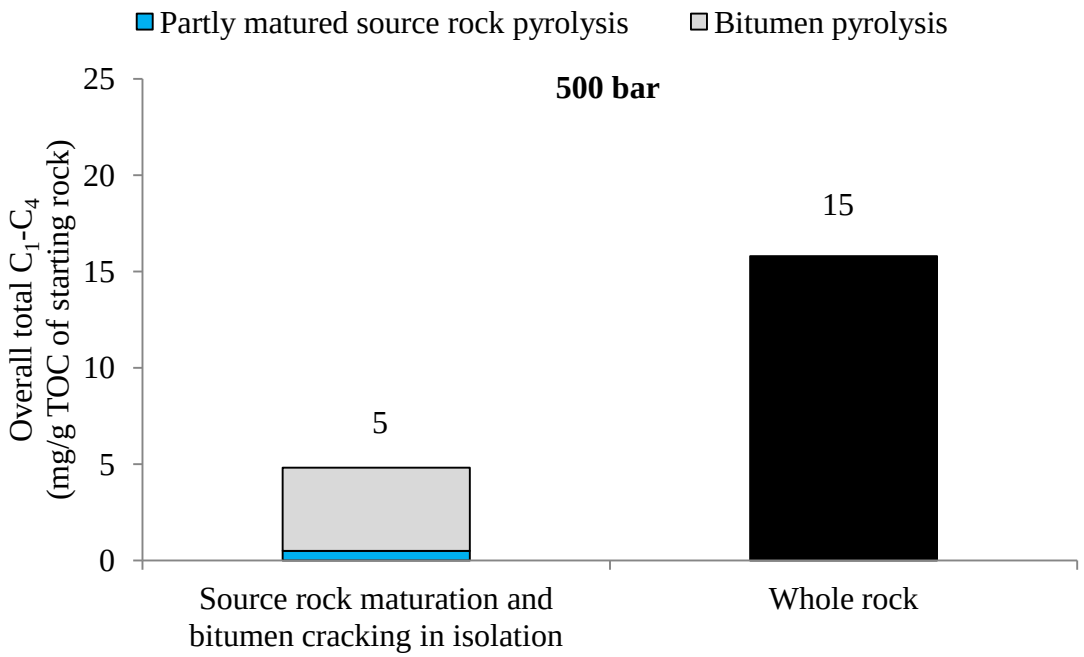

Fig. 5.2b. Total gas yields at 500 bar at 350 °C for 24 h (25 % TOC set).

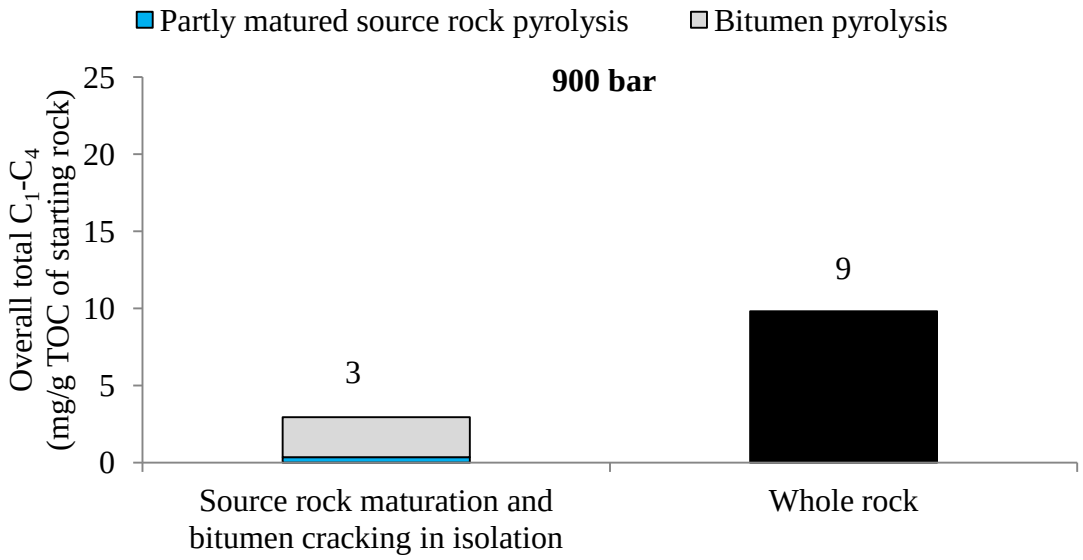

Fig. 5.3. Total gas yields at 900 bar at 350 °C for 24 h (25 % TOC set).

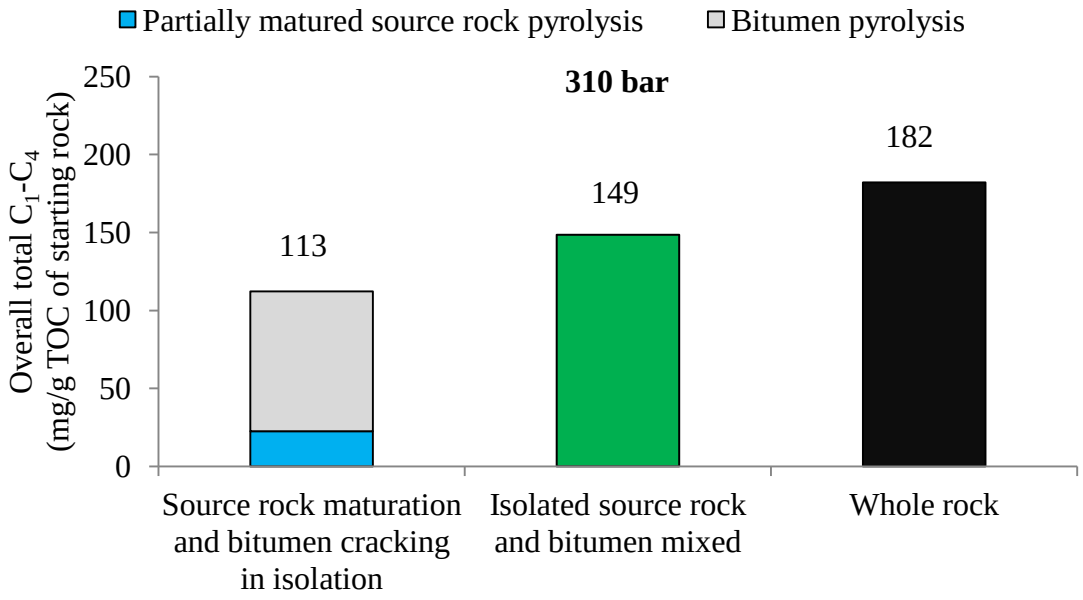

Fig. 5.4a. Total gas yields at 310 bar at 420 °C for 24 h (14 % TOC set).

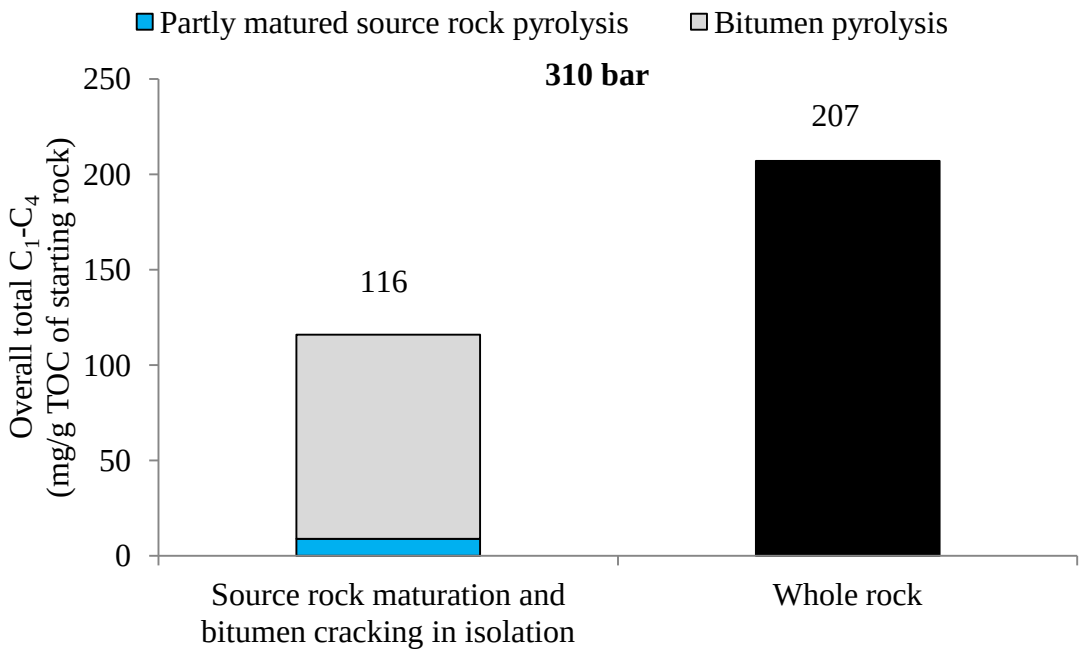

Fig. 5.4b. Total gas yields at 310 bar at 420 °C for 24 h (25 % TOC set).

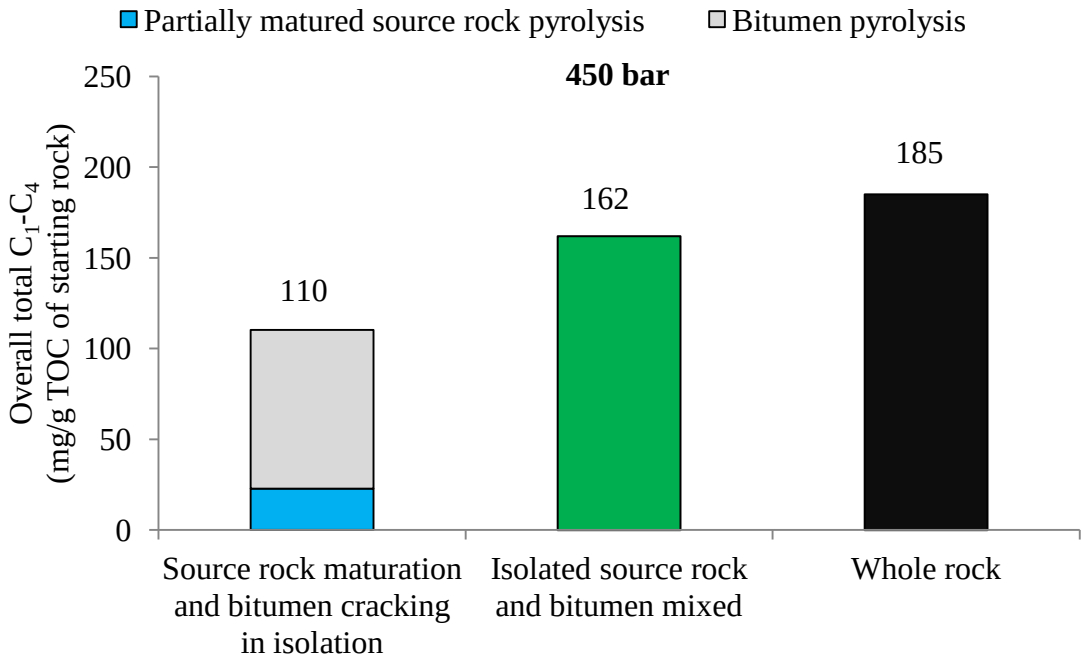

Fig. 5.5a. Total gas yields at 450 bar at 420 °C for 24 h (14 % TOC set).

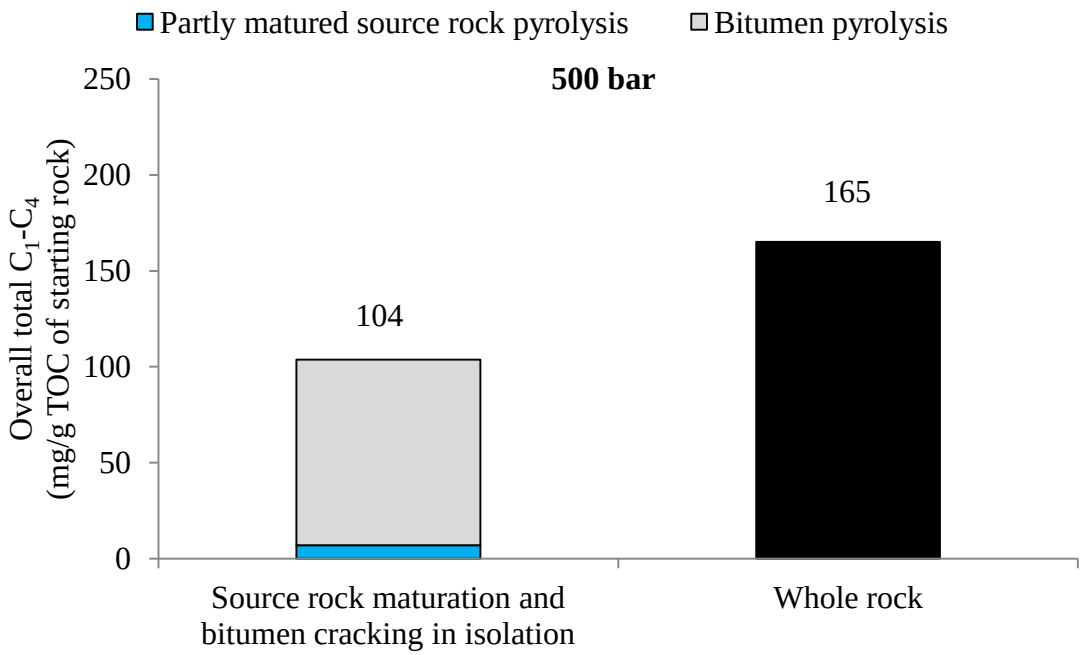

Fig. 5.5b. Total gas yields at 500 bar at 420 °C for 24 h (25 % TOC set).

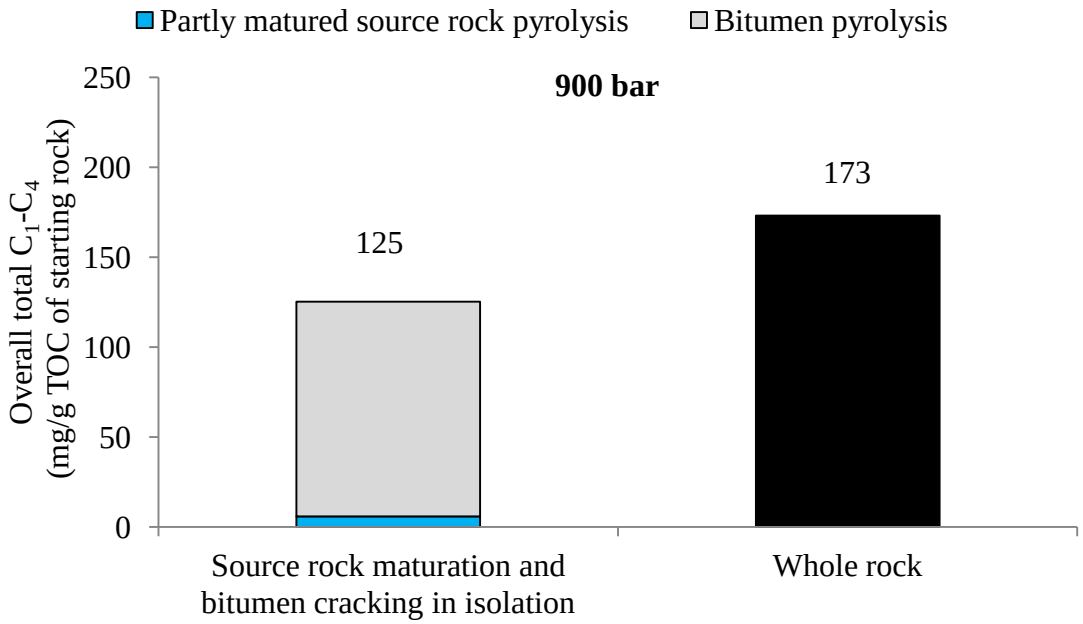

Fig. 5.6. Total gas yields at 900 bar at 420 °C for 24 h (25 % TOC set).

5.2. Bitumen plus oil yields.

Figures 5.7 to 5.12 compares the total bitumen plus oil yields for pyrolysis at 350 and 420 °C for 24 h at low and high pressure from the 14 and 25 % TOC set of whole rock, isolated partially matured source rock and bitumen (isolated fractions) and their recombined mixture experiments. At 350 °C for 24 h, the bitumen plus oil yields (Fig. 5.7a) at 180 bar from the 14 % TOC isolated fraction, recombined mixtures and whole rock experiments were 661, 464 and 563 mg/g TOC, respectively (Fig. 5.7a). Under the same experimental conditions from the 25 % TOC source rocks (180 bar at 350 °C), the bitumen plus oil generated from the whole rock (576 mg/g TOC) is 29 % less than the isolated fraction (808 mg/g TOC) experiment (Fig. 5.7b). At 350 °C and 500 bar (Fig. 5.8a) the bitumen plus oil yield generated from the 14 % TOC source rocks are 688, 438 and 609 mg/g TOC from the isolated fraction, recombined mixtures and whole rock experiments, respectively. For the 25 % TOC high pressure experiments at 350 °C for 24 h, the bitumen plus oil yields from the whole rock experiments were approx. 23 % and 30 % lower at 500 bar (Fig. 5.8b) and 900 bar (Fig. 5.9), respectively, compared to the isolated fraction experiments. The higher bitumen plus oil yield remaining from the isolated fraction experiments indicates that there is less cracking of the bitumen to generate hydrocarbon gas compared to whole rock experiments, where hydrocarbon gas generation are facilitated due to close interactions between the reactant phases (kerogen, bitumen and mineral matter), resulting in lower bitumen plus oil yields from the whole rock experiments compared to the isolated fractions experiments.

At 420 °C for 24 h, the bitumen plus oil yields for the whole rock experiments were also lower at 310 bar (Fig. 5.10a) and 450 bar (Fig. 5.11a) from the 14 % TOC source rocks, and at 310 bar (Fig. 5.10b) from the 25 % TOC source rocks, compared to the isolated fraction experiments. In the case of the 14 % TOC source rocks at 420 °C for 24 h, the whole rock experiments generated 79 mg/g TOC less bitumen plus oil yields compared to the isolated fractions at 310 bar (Fig. 5.10a), whereas at 450 bar at 420 °C for 24 h (Fig. 5.11a) the bitumen plus oil yields is 64 mg/g TOC less compared to the isolated fractions. In the case of the 25 % TOC source rocks at 420 °C for 24 h, the whole rock

experiments generates 49 mg/g TOC less bitumen plus oil yields compared to the isolated fractions at 310 bar (Fig. 5.10b). This implies that there is less cracking of the bitumen to generate hydrocarbon gas from the isolated fractions compared to whole rock experiments, due to the close interactions between the reactant phases (kerogen, bitumen and mineral matter) from the whole rock experiments.

However, at 500 bar (Fig. 5.11b) and 900 bar (Fig. 5.12) at 420 °C for 24 h, there is more bitumen plus oil yield remaining from the whole rock compared to the isolated fraction experiments. This is due to the supercritical water conditions present at 500 and 900 bar from the whole rock experiments favouring the reaction path of whole rock to expel more bitumen plus oil, whereas at 310 bar (under superheated steam) bitumen is directly cracked to gas and pyrobitumen or coke. Furthermore, the lower bitumen plus oil yield generated from the isolated fraction experiments at 500 bar (Fig. 5.11b) and 900 bar (Fig. 5.12) at 420 °C under the same experimental conditions is due to the bitumen in the isolated fractions being more conveniently cracked to gas and pyrobitumen as bitumen is already present during the beginning of the isolated fraction experiments compared to the whole rock experiments. In the case of whole rock experiments the bitumen has to be formed first before it is further cracked to gas, oil and pyrobitumen. The effect of supercritical water present at 500 and 900 bar combined with the late generation of bitumen from the whole rock experiments is the reason why more bitumen plus oil yield remains from the whole rock experiments at 500 bar (Fig. 5.11b) and 900 bar (Fig. 5.12) compared to the isolated fractions, which is in contrast to the previous experiments shown in Fig. 5.7a to 5.11a.

In the case of the recombined mixture experiments, the bitumen plus oil yields were always lower compared to the whole rock and the isolated fraction experiments (Figs. 5.7a, 5.8a, 5.10a and 5.11a). This is due to the bitumen being strongly adsorbed to the partially matured source rock, which is consistent with the higher residual rock TOC (indicating more coke formed) from the recombined mixtures experiments compared to

the whole rock experiment under the same experimental conditions. Overall, the bitumen plus oil yields were always lower for the whole rock experiments compared to the isolated fraction experiments apart from the 25 % TOC source rocks at 420 °C and 500 bar (Fig. 5.11b) and 900 bar (Fig. 5.12), whereas the recombined mixture experiments always generate the lowest bitumen plus oil yield.

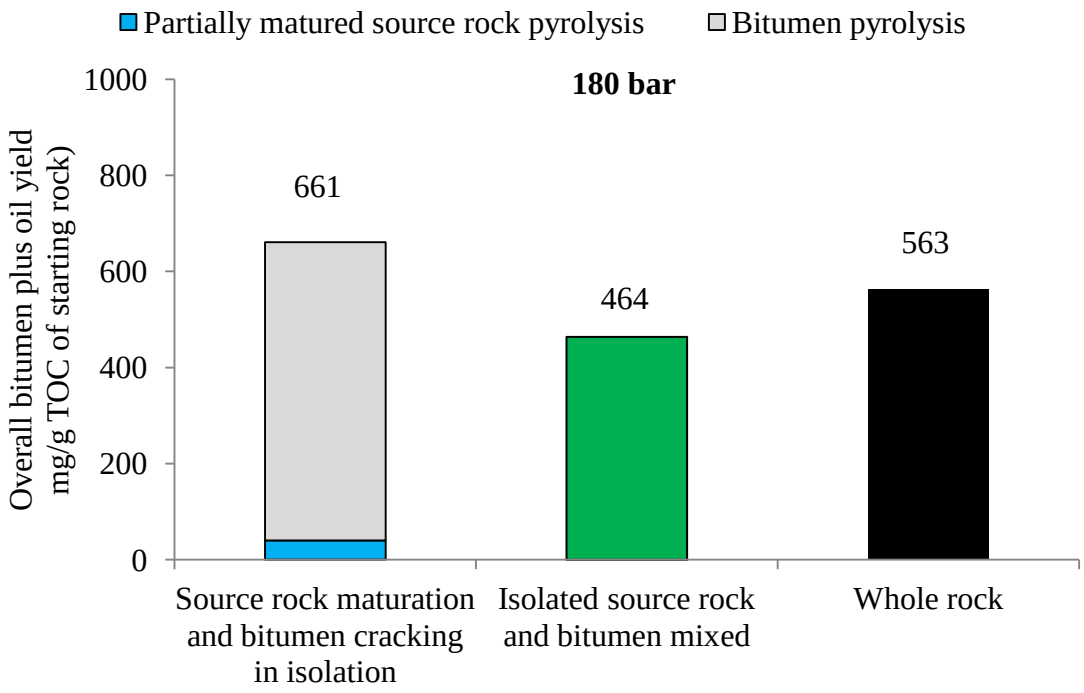

Fig. 5.7a. Total bitumen plus oil yields at 180 bar at 350 °C for 24 h (14 % TOC set).

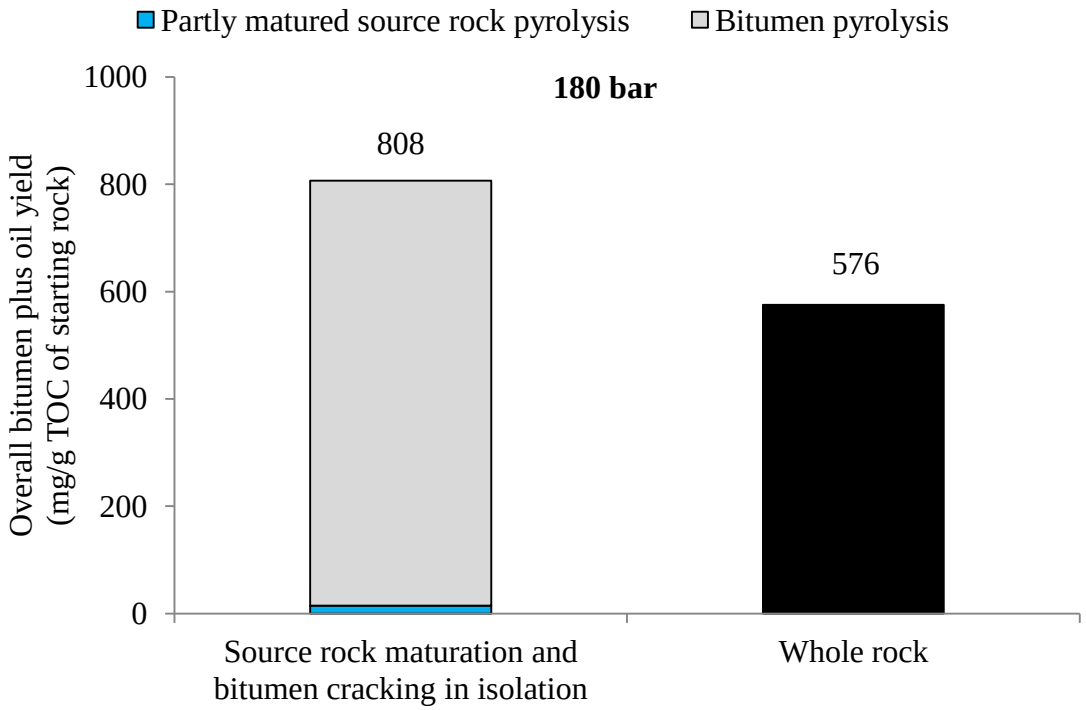

Fig. 5.7b. Total bitumen plus oil yields at 180 bar at 350 °C for 24 h (25 % TOC set).

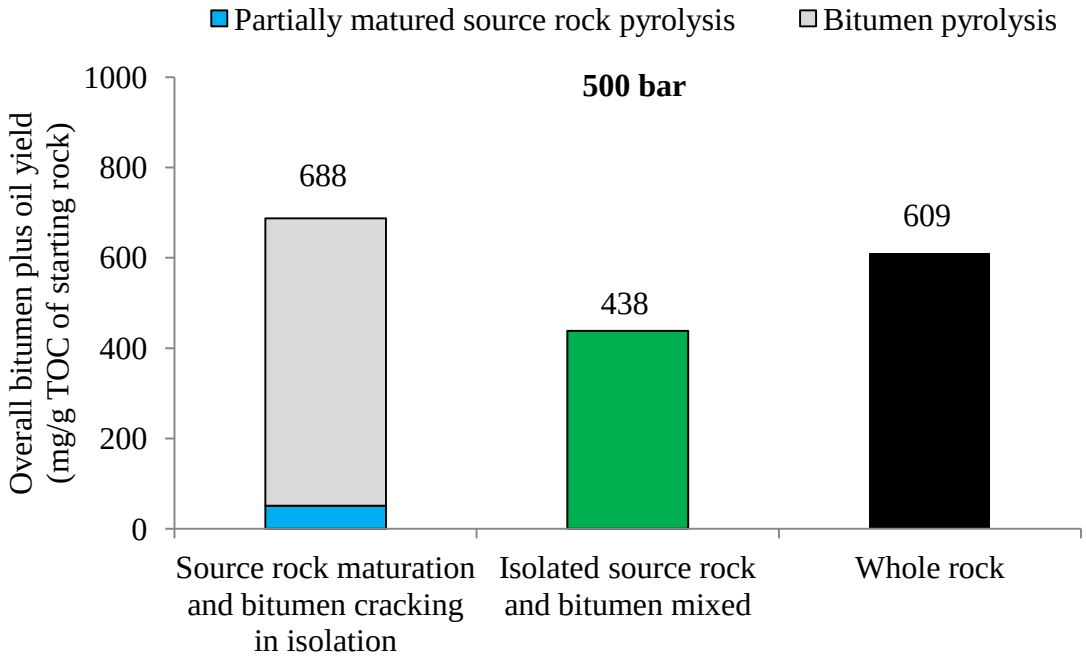

Fig. 5.8a. Total bitumen plus oil yields at 500 bar at 350 °C for 24 h (14 % TOC set).

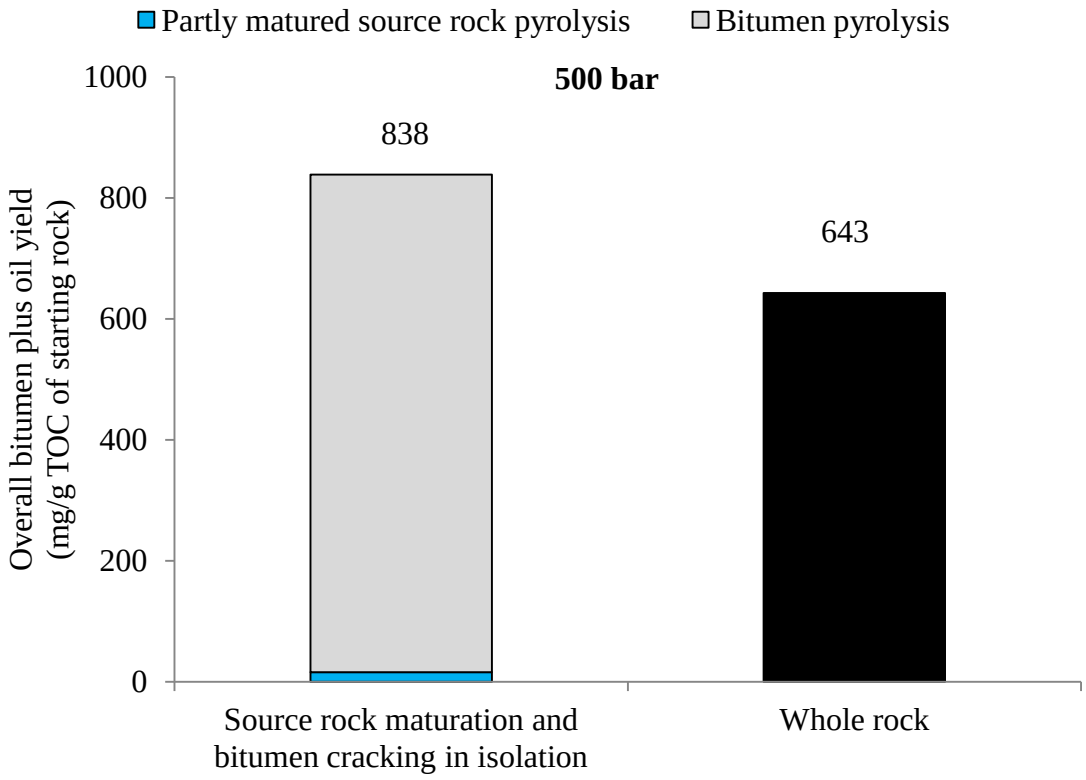

Fig. 5.8b. Total bitumen plus oil yields at 500 bar at 350 °C for 24 h (25 % TOC set).

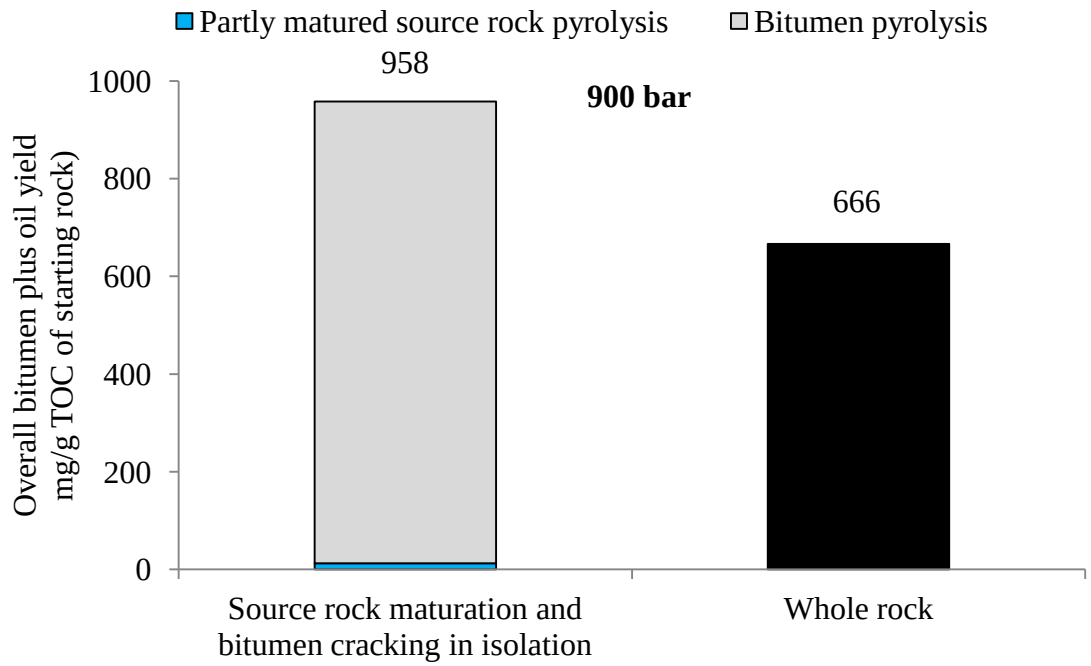

Fig. 5.9. Total bitumen plus oil yields at 900 bar at 350 °C for 24 h (25 % TOC set).

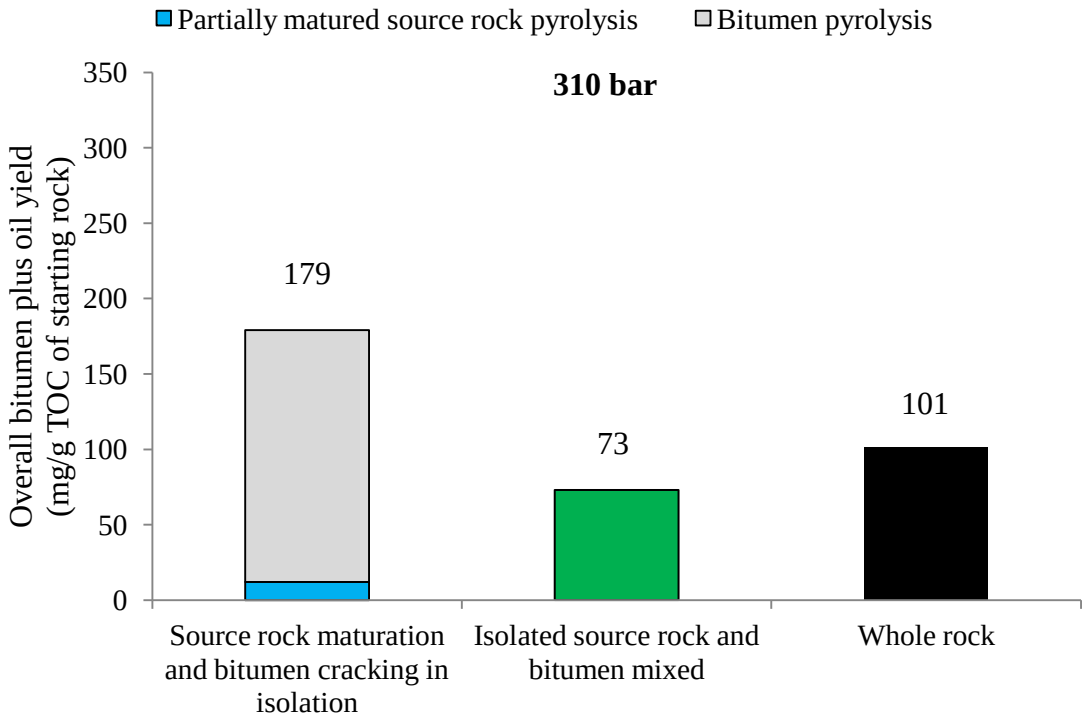

Fig. 5.10a. Total bitumen plus oil yields at 310 bar at 420 °C for 24 h (14 % TOC set).

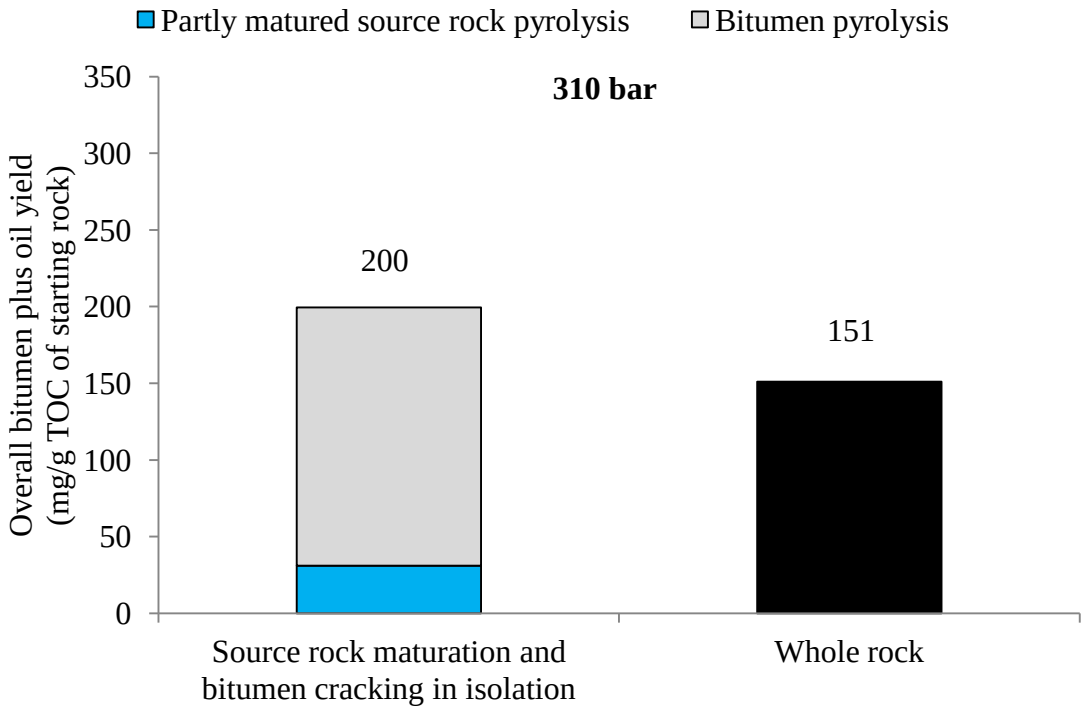

Fig. 5.10b. Total bitumen plus oil yields at 310 bar at 420 °C for 24 h (25 % TOC set).

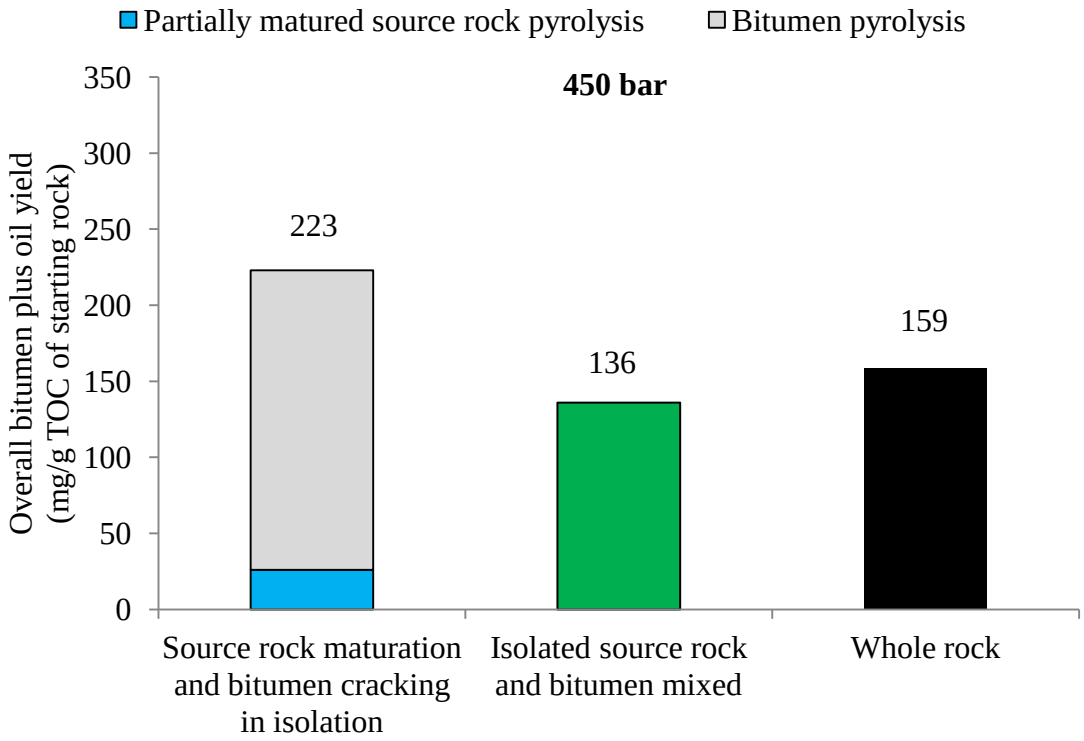

Fig. 5.11a. Total bitumen plus oil yields at 450 bar at 420 °C for 24 h (14 % TOC set).

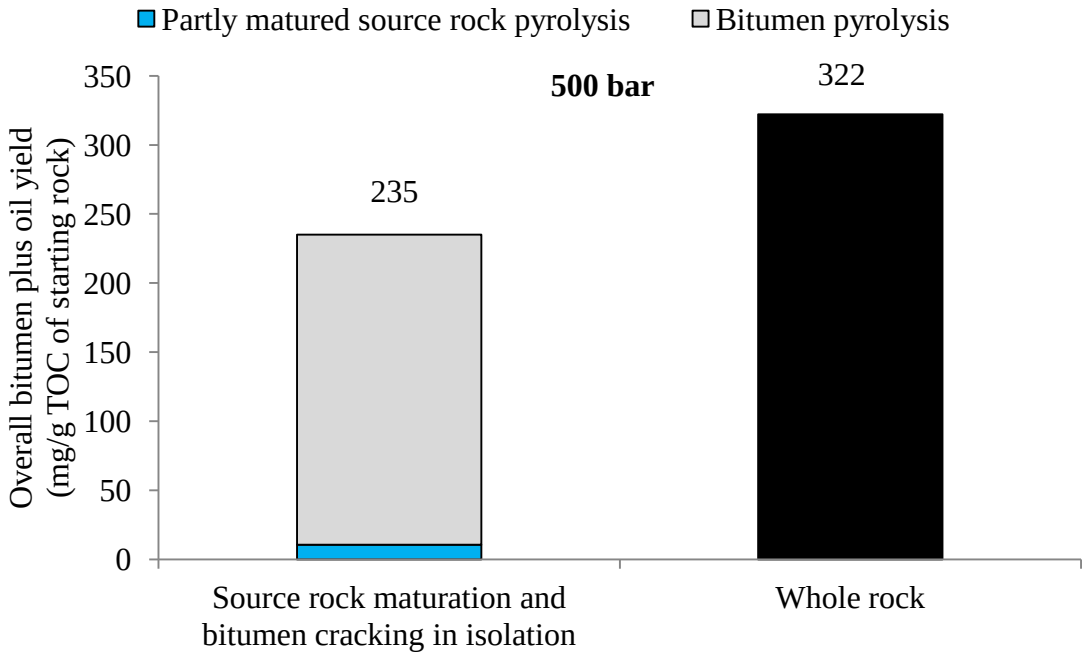

Fig. 5.11b. Total bitumen plus oil yields at 500 bar at 420 °C for 24 h (25 % TOC set).

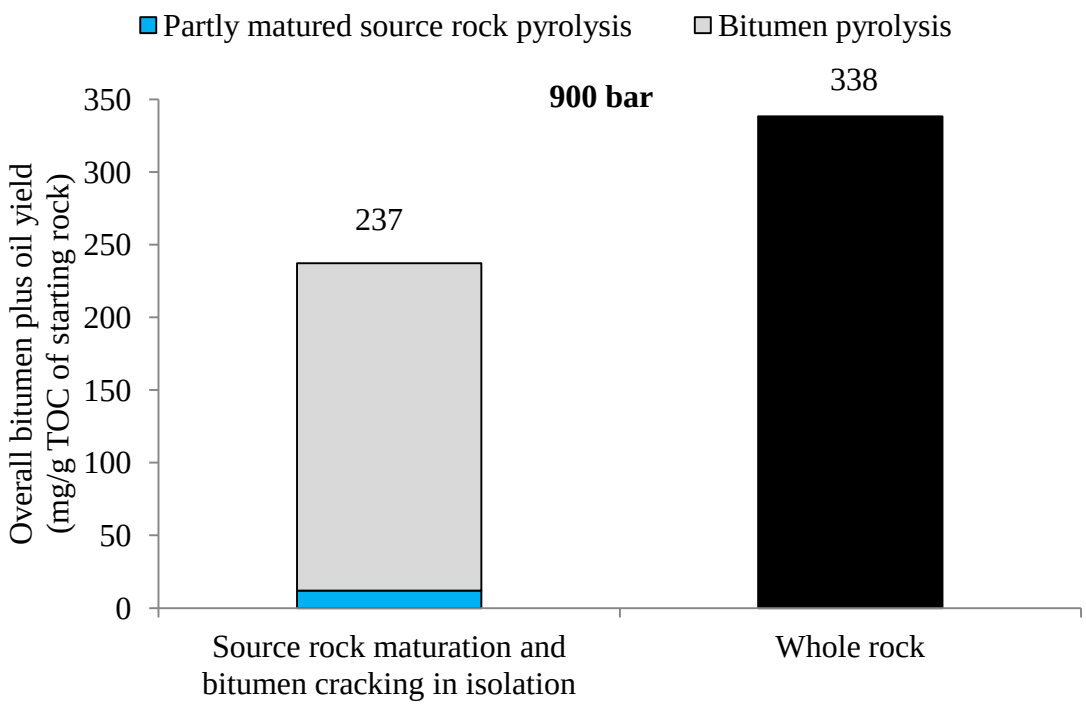

Fig. 5.12. Total bitumen plus oil yields at 900 bar at 420 °C for 24 h (25 % TOC set).

5.3. Coke yields.

Figures 5.13 to 5.15 and Tables 5.1 to 5.6 compares the coke yields for pyrolysis at 420 °C for 24 h at low (310 bar) and high pressure (500 and 900 bar) from the 14 and 25 % TOC set of whole rock, isolated partially matured source rock and bitumen (isolated fractions) and their recombined mixture experiments. The coke yields generated from the 14 % TOC isolated fractions, recombined mixtures and whole rock experiments were 530, 509 and 524 mg/g TOC, respectively at 310 bar (Fig. 5.13a), whereas from the 25 % TOC source rocks under the same conditions (310 bar at 420 °C for 24 h) the whole rock experiments (415 mg/g TOC) generated less coke than the isolated fraction experiments (521 mg/g TOC) as shown in (Fig. 5.13b). At 450 bar (Fig. 5.14a) the coke yields from the 14 % TOC set of experiments were 522, 481, 446 mg/g TOC for the isolated fractions, recombined mixtures and whole rock experiments, respectively. In the case of the 25 % TOC high pressure experiments at 350 °C for 24 h, the coke yields from the whole rock experiments were approx. 2 folds lower at 500 bar (Fig. 5.14b) and 900 bar (Fig. 5.15), compared to the isolated fractions experiment. Figures 5.13 to 5.15 indicate that the coke is mainly generated from the isolated bitumen cracking experiments for the 25 % TOC source rocks, whereas equal amounts of coke was contributed for the 14 % TOC isolated partially matured source rock and bitumen cracking experiments in comparison to the whole rock experiments. The higher coke yields generated from the 25 % TOC bitumen cracking experiments (Figs. 5.13b and 5.14b) is due to more initial bitumen at the start of the experiment (1.0 g) compared to the 14 % TOC bitumen cracking experiments (Figs. 5.13a and 5.14a).

Overall, the highest coke yields are always generated from the isolated fractions experiment due to direct cracking of the already formed bitumen plus oil into coke, whereas in the case of the whole rock experiments, bitumen plus oil needs to be generated first before it can be cracked to coke. In addition, the large difference in coke yields between the 500 and 900 bar whole rock experiments compared to the isolated fractions experiment at 420 °C (Fig. 5.14b and 5.15) is due to the supercritical water conditions (present at 500 and 900 bar) facilitating bitumen cracking to oil rather than coke for the whole rock experiments.

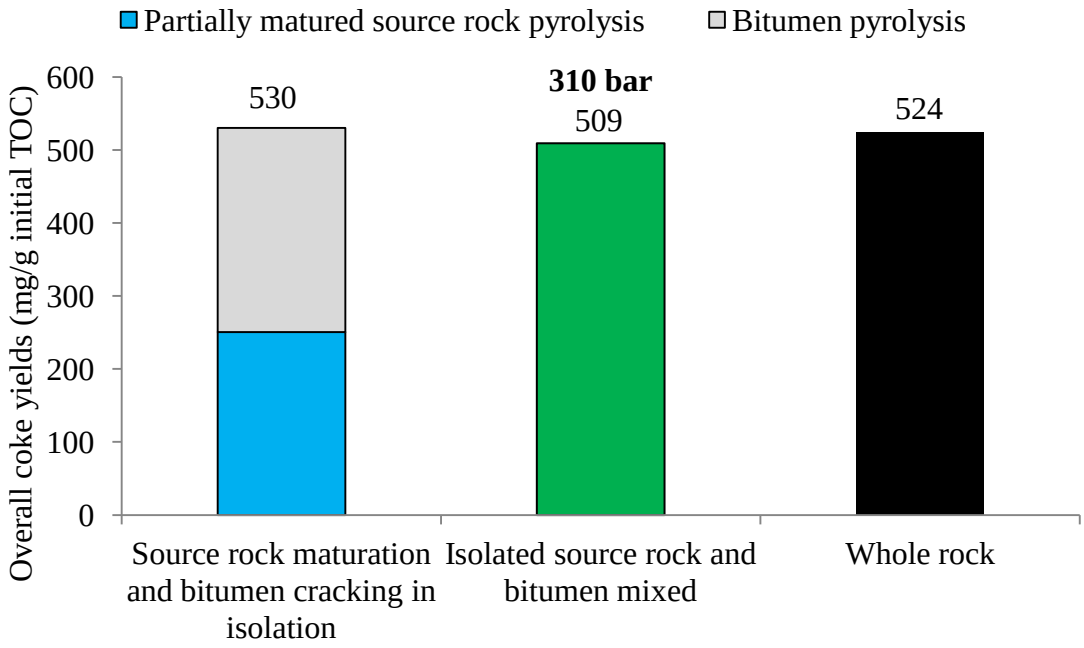

Fig. 5.13a. Total coke yields at 310 bar at 420 °C for 24 h (14 % TOC set).

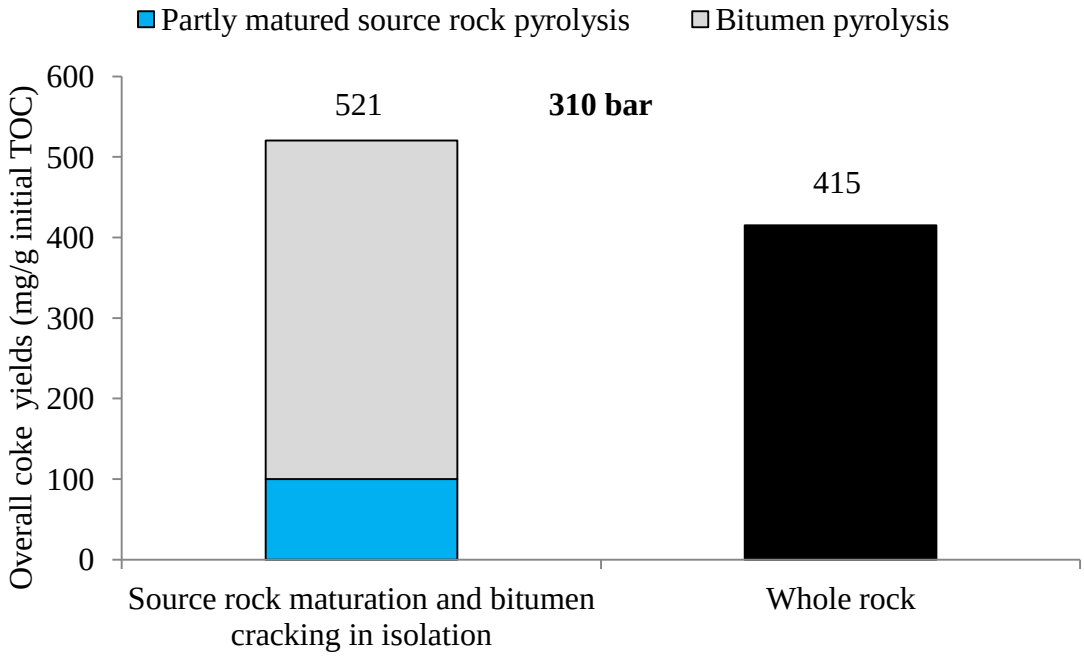

Fig. 5.13b. Total coke yields at 310 bar at 420 °C for 24 h (25 % TOC set).

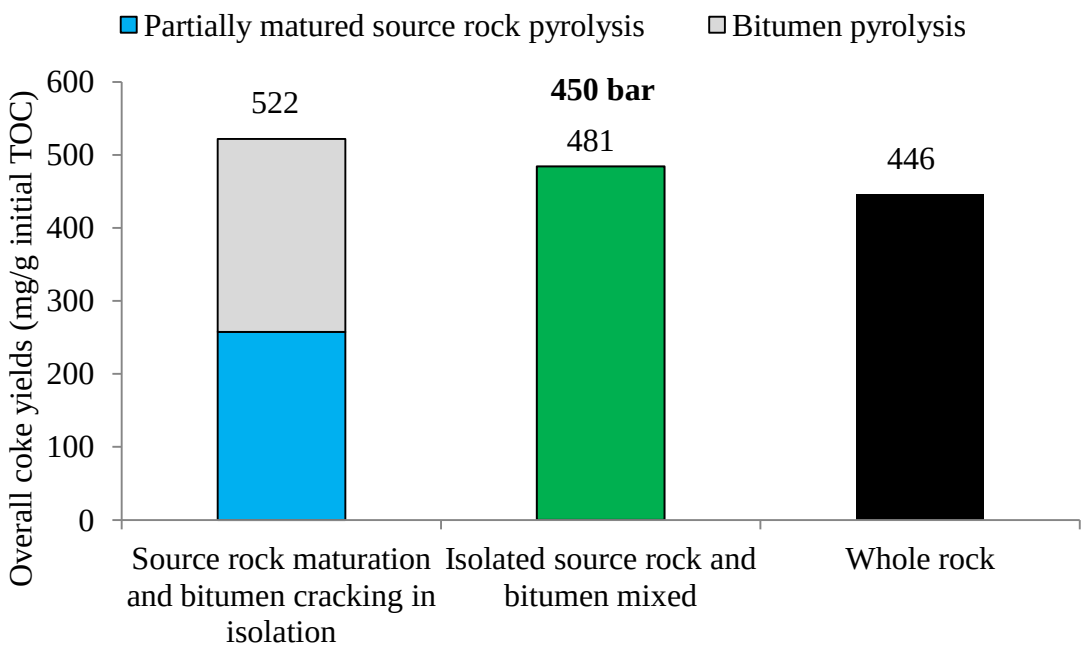

Fig. 5.14a. Total coke yields at 450 bar at 420 °C for 24 h (14 % TOC set).

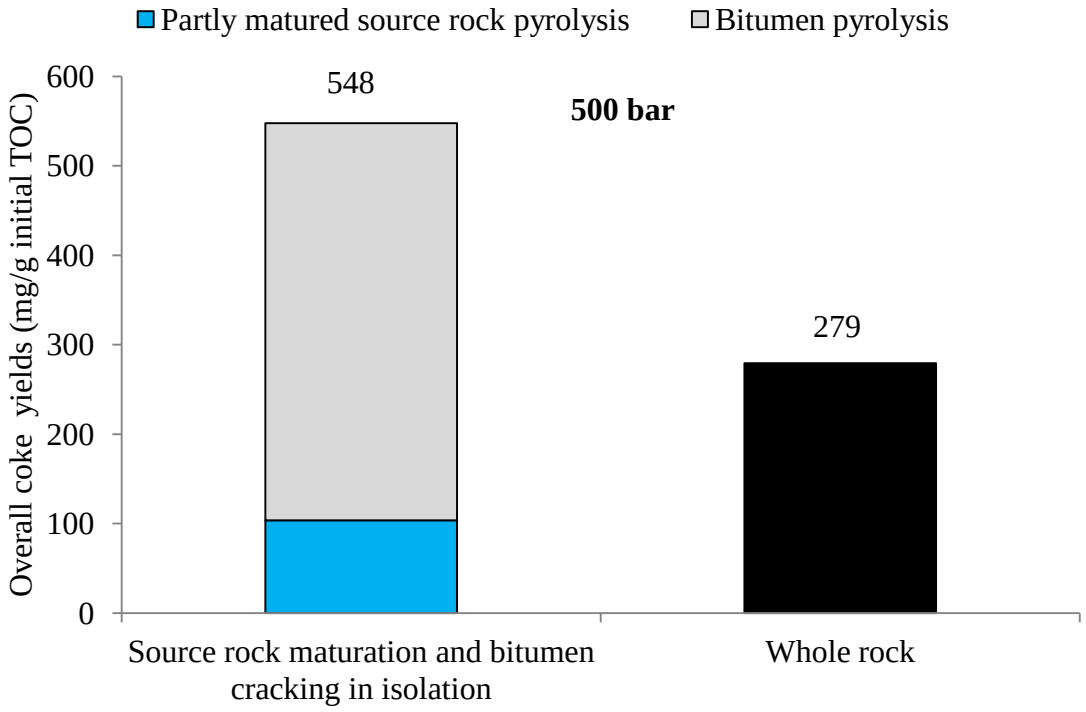

Fig. 5.14b. Total coke yields at 500 bar at 420 °C for 24 h (25 % TOC set).

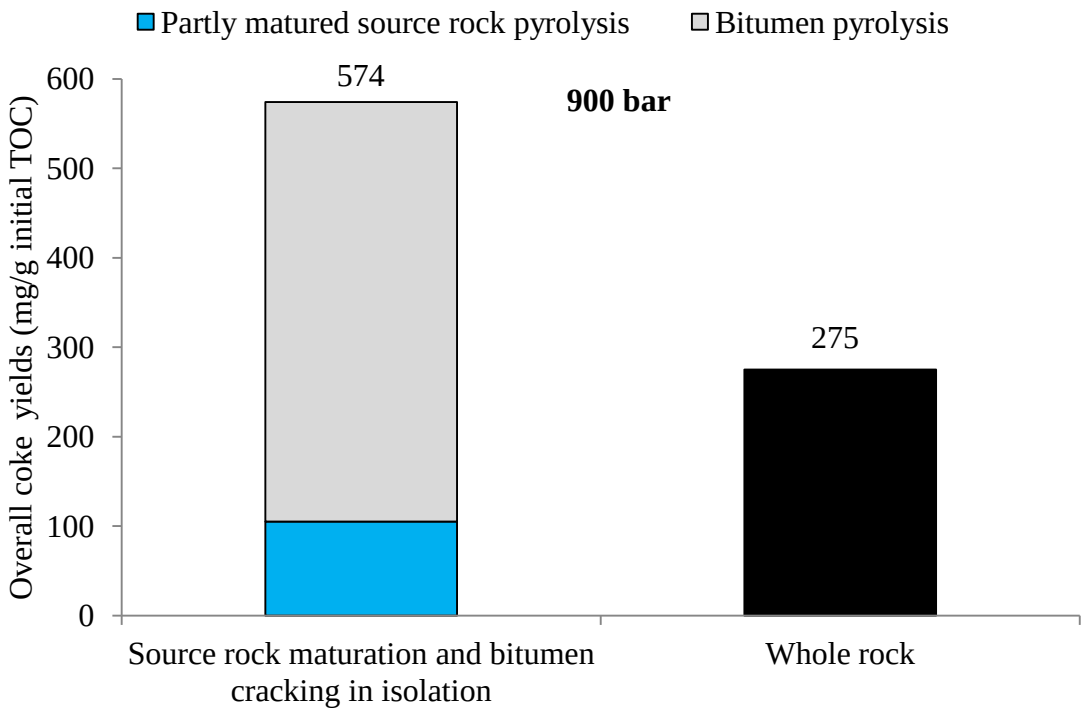

Fig. 5.15. Total coke yields at 900 bar at 420 °C for 24 h (25 % TOC set).

5.4. Biomarker ratios.

The biomarker ratios from the 14 % TOC set of whole rock, recombined mixtures and bitumen pyrolysis in isolation at 350 °C for 24 h are presented in Table 5.7. The biomarker ratios from a 14 % TOC partially matured source rock experiments at 180 bar and 350 °C for 24 h were also included in Table 5.7.

At 180 bar, the lowest Pr/nC_{17} (0.28) and Ph/nC_{18} (0.20) ratios from the partially matured source rock indicate that the bitumen plus oil has the highest maturity and fastest thermal cracking compared to the whole rock, recombined mixtures and isolated bitumen cracking experiments. The Pr/nC_{17} (1.59) and the Ph/nC_{18} (1.53) ratios from the recombined mixture experiments shows the second highest maturity and thermal cracking among the experiments conducted at 180 bar at 350 °C for 24 h. The higher Pr/nC_{17} ratio from the whole rock (1.92) indicates that a less mature bitumen plus oil was obtained from the whole rock compared to bitumen pyrolysed individually (1.68), whereas the Ph/nC_{18} indicate similar maturities were obtained between the whole rock (1.68) and bitumen pyrolysed individually (1.72). Overall at 180 bar, the Pr/nC_{17} and the Ph/nC_{18} indicates faster bitumen cracking reaction are occurring for experiments with partially matured source rock and recombined mixtures compared to whole rock and isolated bitumen cracking experiments.

When comparing C_{29} and C_{30} $\beta\alpha/\alpha\beta$ hopane ratios at 180 bar, the results indicate that the highest maturities were achieved from the recombined mixtures (C_{29} $\beta\alpha/\alpha\beta$ = 0.11 and C_{30} $\beta\alpha/\alpha\beta$ = 0.19) and the lowest were from the bitumen pyrolysed individually (C_{29} $\beta\alpha/\alpha\beta$ = 0.43 and C_{30} $\beta\alpha/\alpha\beta$ = 0.46). Similar maturities were shown from the bitumen plus oil sample for the whole rock (C_{29} $\beta\alpha/\alpha\beta$ = 0.25 and C_{30} $\beta\alpha/\alpha\beta$ = 0.33) and the partially matured source rock (C_{29} $\beta\alpha/\alpha\beta$ = 0.25 and C_{30} $\beta\alpha/\alpha\beta$ = 0.35) experiments. The C_{31} and C_{32} S/(S+R) hopane ratios indicate a higher maturity was obtained from the bitumen plus oil sample for the whole rock (C_{31} S/(S+R) = 0.54 and C_{32} S/(S+R) = 0.54), recombined mixtures (C_{31} S/(S+R) = 0.60) and partially matured source rock (C_{31} S/(S+R) = 0.59 and C_{32} S/(S+R) = 0.60) experiments compared to the isolated bitumen

cracking experiments (C_{31} S/(S+R) = 0.47 and C_{32} S/(S+R) = 0.42), apart from the ratios which are not determined due to a high level of noise on these peaks.

At 500 bar at 350 °C for 24 h, the same trend was observed where the Pr/nC_{17} biomarkers ratio indicates that the highest maturity and faster thermal cracking was obtained from the recombined mixtures (Pr/nC_{17} = 1.60), whereas the Ph/nC_{18} biomarkers ratio indicate similar maturities were achieved between the whole rock (Ph/nC_{18} = 1.77) and recombined mixtures experiments (Ph/nC_{18} = 1.77). The C_{29} $\beta\alpha/\alpha\beta$ hopane ratios shows a less matured bitumen plus oil was obtained from whole rock experiments (C_{29} $\beta\alpha/\alpha\beta$ = 0.33) compared to the recombined mixture (C_{29} $\beta\alpha/\alpha\beta$ = 0.12). The lower C_{29} and C_{30} hopanes at 500 bar from the whole rock and recombined mixtures imply that when bitumen is cracked in the presence of the source rocks (whole rock, partially matured source rock and recombined mixtures), isomerisation of the C_{29} and C_{30} hopanes in the bitumen plus oil is enhanced compared to bitumen cracking in isolation. The C_{31} and C_{32} S/(S+R) hopane ratios at 500 bar follows the same trend where the recombined mixtures shows the highest maturity, whereas bitumen cracking in isolation generated the least mature bitumen plus oil.

Overall, the extent of cracking and isomerisation is highest for the partially matured source rock, possibly due to the extensive amount of clay to the remaining bitumen in the partially matured source rock. The recombined mixtures also show higher level of maturity compared to the whole rock experiments. This might be due to longer residence time experienced by the bitumen plus oil in the recombined mixtures (340 °C for 7 h from bitumen generation plus 24 h) compared to the bitumen in the whole rocks (24 h). Although the extent of cracking and isomerisation at 350 °C are quite mild, a clear trend is observed where higher maturities were obtained when bitumen is cracked in close interactions with the kerogen/source rock and mineral matter compared to the bitumen pyrolysed individually.

Table 5.7. Biomarker ratios (Pr/nC_{17} and Ph/nC_{18} ratios, the C_{29} and C_{30} $\beta\alpha/\alpha\beta$ hopane ratios, and the C_{31} and C_{32} $\alpha\beta$S/($\alpha\beta$S + $\alpha\beta$R) hopane ratios for 14 % TOC set of experiments (14 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Time (h)	Isoprenoids		Hopanes			
				Pr/nC_{17}	Ph/nC_{18}	C_{29} $\beta\alpha/\alpha\beta$	C_{30} $\beta\alpha/\alpha\beta$	C_{31} S/(S+R)	C_{32} S/(S+R)
Low Pressure									
Whole rock	180	350	24	1.92	1.68	0.25	0.33	0.54	0.54
Recombine Mixtures	180	350	24	1.59	1.53	0.11	0.19	0.60	Not Determined
Partially matured source rock pyrolysis	180	350	24	0.28	0.20	0.25	0.35	0.59	0.60
Bitumen Pyrolysis	180	350	24	1.68	1.72	0.43	0.46	0.47	0.42
High Pressure									
Whole rock	500	350	24	1.93	1.77	0.33	0.37	0.53	0.51
Recombine Mixtures	500	350	24	1.60	Not Determined	0.12	Not Determined	0.58	0.57
Bitumen Pyrolysis	500	350	24	1.85	1.77	0.45	0.49	0.48	0.44

5.5. Vitrinite reflectances.

Figures 5.16 to 5.19 shows the vitrinite reflectance (VR) plots of the source rock residues from the 14 % TOC set of whole rock and isolated partially matured source rock experiment (source rock in isolation). The VR of the 14 % TOC source rocks is higher from the whole rock experiments compared to the isolated partially matured source rock experiments for all the experimental conditions. At 350 °C under 180 bar (Fig. 5.16) and 420 °C under 310 bar conditions (Fig. 5.18) the VR is about 0.2 % Ro higher from the whole rock compared to the isolated partially matured source rock. At high pressure (450-500 bar), the VR values were 0.1 % and 0.2 % Ro higher at 350 and 420 °C, respectively, for whole rock experiments compared to partially matured source rock experiments (Figs. 5.17 and 5.19). The higher VR observed at both 350 and 420 °C for whole rock experiments are even more pronounced when the VR of the starting rock is considered, for example at 350 °C under 180 bar hydrous conditions, the VR increased from 0.3 % Ro (initial rock) to 1.5 % Ro (whole rock), while for the isolated source rock, the VR only increased to 1.3 % Ro from about 0.9 % Ro (partially matured rock). At 500 bar and 350 °C (Fig. 5.17), the VR increased to 1.0 % Ro from the starting rock for the whole rock experiment, while for partially matured source rock experiments the VR was 0.9 % Ro, the same as the starting partially matured rock. Overall, the higher VR observed for whole rock experiments shows that source rock maturation is promoted in the presence of bitumen. This might be due to the presence of bitumen facilitating free radical transfer reactions resulting in aromatisation reactions occurring to a greater extent in the whole rock experiments compared to the partially matured source rock experiments.

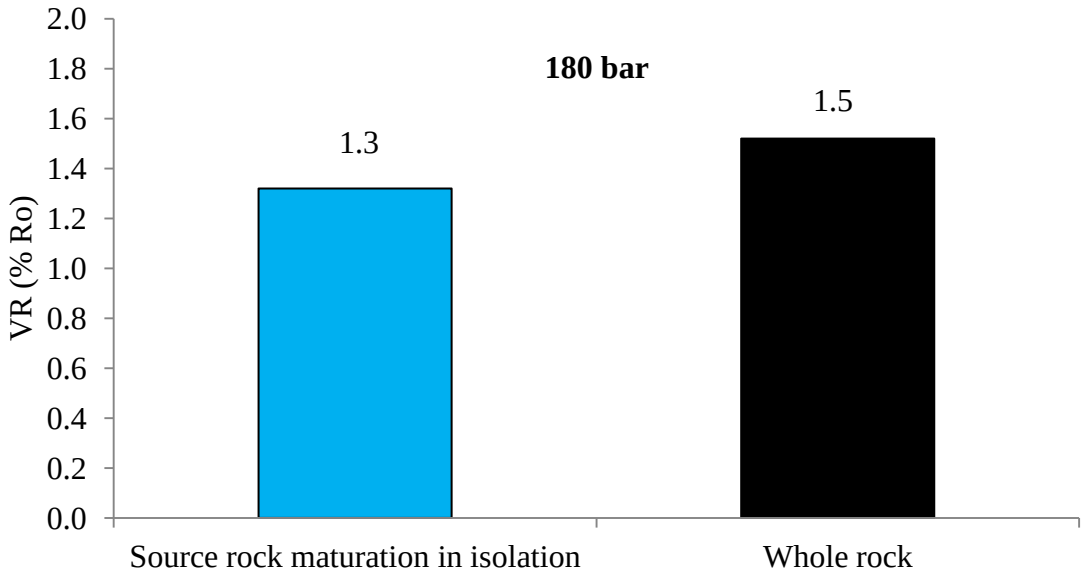

Fig. 5.16. Vitrinite reflectance (% Ro) at 180 bar at 350 °C for 24 h (14 % TOC set).

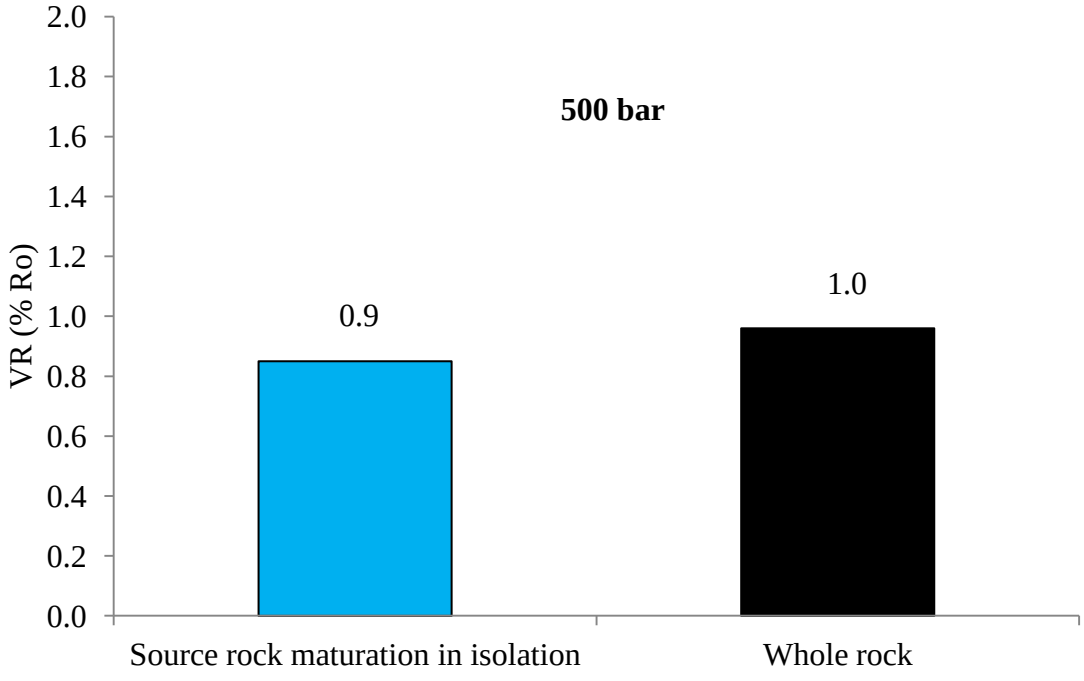

Fig. 5.17. Vitrinite reflectance (% Ro) at 500 bar at 350 °C for 24 h (14 % TOC set).

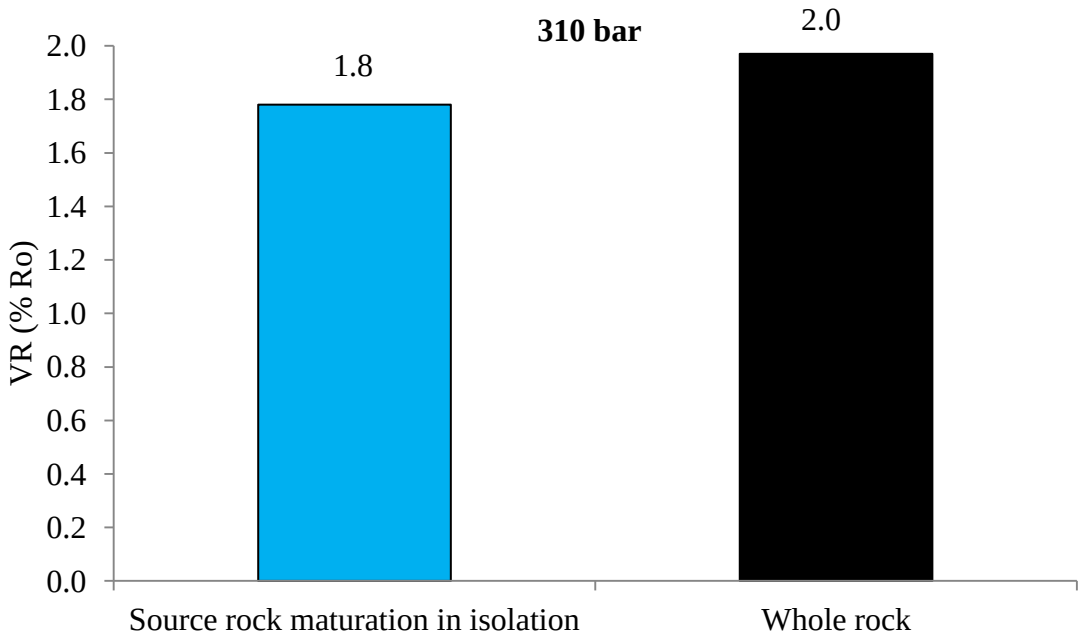

Fig. 5.18. Vitrinite reflectance (% Ro) at 310 bar at 420 °C for 24 h (14 % TOC set).

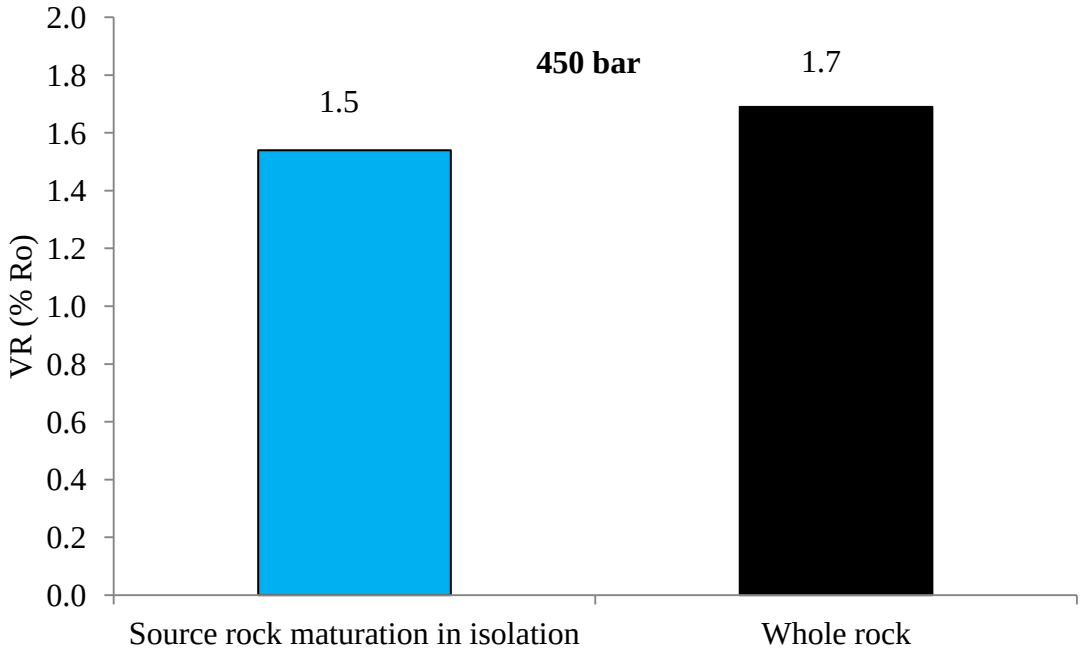

Fig. 5.19. Vitrinite reflectance (% Ro) at 450 bar at 420 °C for 24 h (14 % TOC set).

5.6. Comparing powdered and rock chip experiments at 450 bar and 420 °C for 24 h.

This study was conducted in order to study the effects of particle size on hydrocarbon generation. Figures 5.20 to 5.23 and Tables 5.8 to 5.10 shows the total gas C_1-C_4 gas, gas dryness ratio, bitumen plus oil yields, residual rock mass (g) and/or coke yields for pyrolysis at 420 °C for 24 h at high pressure (450 bar) from the 30 % TOC source rocks experiments. The results from the 30 % TOC whole rock, isolated partially matured source rock and bitumen (isolated fractions) and their recombined mixture experiments are listed in Tables 5.8 to 5.10, respectively. The average amount of gas, bitumen and partially matured source rock generated from a 30 % TOC bitumen generation experiment is approx. 12 mg/g TOC, 1.0 g/g TOC and 2.0 g/g TOC, respectively (Table 4.9c, previously). The yields in Tables 5.8 to 5.10 also contain summations of hydrocarbon yields from three components (bitumen generation, isolated partially matured source rock and bitumen cracking and in recombined mixtures), while the plots in Figures 5.20 to 5.23 only contains two components (excluding bitumen generation yields).

Table 5.8. Total gas (mg/g initial TOC), gas dryness ratio ($C_1/(C_1\text{-}C_4)$) ratio, bitumen plus oil yields (mg/g TOC), residual rock mass (g) and residual rock TOC (%) from duplicate experiments (1 and 2) for the rock chip whole rock experiments at 420 °C for 24 h (30 % TOC set).

Experiment	Pressure (bar)	Temp (°C)	Total ($C_1\text{-}C_4$)	$\frac{C_1}{(C_1\text{-}C_4)}$	Bitumen plus oil	Residual Rock (g)	Residual Rock TOC (%)
Whole rock 1	450	420	139	0.35	184	2.1	22.2
Whole rock 2	450	420	139	0.35	189	2.1	22.6

Table 5.9. Total gas, bitumen plus oil yields (mg/g of initial TOC), coke yields (mg/g of initial TOC), residual rock TOC (%), initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the isolated partially matured source rock and bitumen pyrolysed individually at low pressure (310 bar) at 420 °C (30 % TOC set).

	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Coke	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
High pressure Experiment								
Bitumen generation[b] 1	180-1	6	350	12			9.2	
Bitumen generation[c] 2	180-2	6	350	12			9.1	
Partially matured source rock pyrolysis 1	450	24	420	8.2	17		8.1	178
Partially matured source rock pyrolysis 2	450	24	420	8.1	19		8.0	176
Bitumen pyrolysis 1	450	24	420	110	216	314		758
Bitumen pyrolysis 2	450	24	420	110	212	311		760
Overall yield (mg/g initial TOC) 1				130	233	314	8.1	
Overall yield (mg/g initial TOC) 2				130	231	311	8.0	

[b and c] Bitumen from experiment 1 and 2 in Table 4.9c, respectively.

Table 5.10. Total gas, bitumen plus oil yields (mg/g of initial TOC), coke yields (mg/g of initial TOC), residual rock TOC (%), initial bitumen and partially matured source rock used (mg of TOC) from duplicate experiments (1 and 2) for the recombine mixture experiments at low pressure (310 bar) at 420 °C (30 % TOC set).

	Pressure (bar)	Time (h)	Temp (°C)	Total (C_1-C_4)	Bitumen plus oil	Residual Rock TOC (%)	Bitumen and source rock (mg of TOC)
High pressure Experiment							
Bitumen generation[b] 1	180-3	6	350	11		9.1	
Bitumen generation[c] 2	180-4	6	350	11		9.2	
Recombined mixture 1	450	24	420	125	217	18.0	177 & 761
Recombined mixture 2	450	24	420	125	212	18.2	178 & 762
Overall yield (mg/g initial TOC) 1				130	217	18.0	
Overall yield (mg/g initial TOC) 2				130	212	18.2	

5.6.1. Gas yields.

Figure 5.20 to 5.23 displays the gas generated from the whole rock, isolated partially matured source rock and bitumen pyrolysis and recombined mixture experiments, respectively, at 420 °C for 24 h. In order to ascertain the effects of particle size on hydrocarbon generation, gas yields on the partially matured source rocks is equated to 1 g TOC of partially matured source rock (Fig. 5.21), instead of initial starting rock.

The total gas yields generated from the 30 % TOC whole rock experiments (139 mg/g TOC) were lower in comparison to the 14 % TOC (191 mg/g TOC) set of whole rock experiments (Fig. 5.20). The set of partially matured source rock experiments (Fig. 5.21) shows higher gas yields were generated from the 14 % TOC partially matured source rock experiments, compared to the 30 % TOC partially matured source rock experiments. This is due to the increased surface area from the powdered experiments (14 % TOC) compared to using rock chips. However, for the recombined mixture experiments (Fig. 5.23), higher gas yields were generated from the 14 % TOC source rocks compared to using the 30 % TOC rock chip samples due to less amount of bitumen adsorbed on the surface of the rock chips compared to using powders (14 % TOC source rocks). In the case of the bitumen cracking experiments (Fig. 5.22), the lower gas yields obtained from the 14 % TOC bitumen (88 mg/g TOC of initial starting rock) is due to lower amounts of initial bitumen used (0.8 g) compared to the 30 % TOC bitumen (0.9 g). Overall, the experiments using powdered samples (14 % TOC) generated more hydrocarbon gas compared to the 30 % TOC set of experiments, where larger sized samples were used. This is due to the increased surface area present in the powdered samples facilitating gas generation compared to the rock chips.

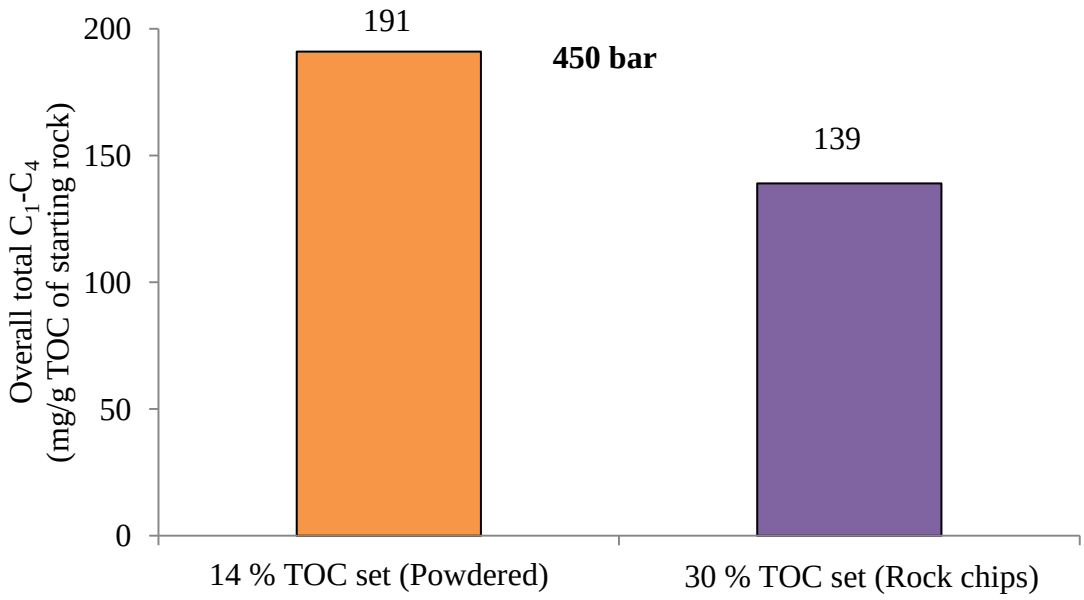

Fig. 5.20. Total gas yields for the 14 and 30 % TOC whole rock experiments at 420 °C for 24 h at 450 bar.

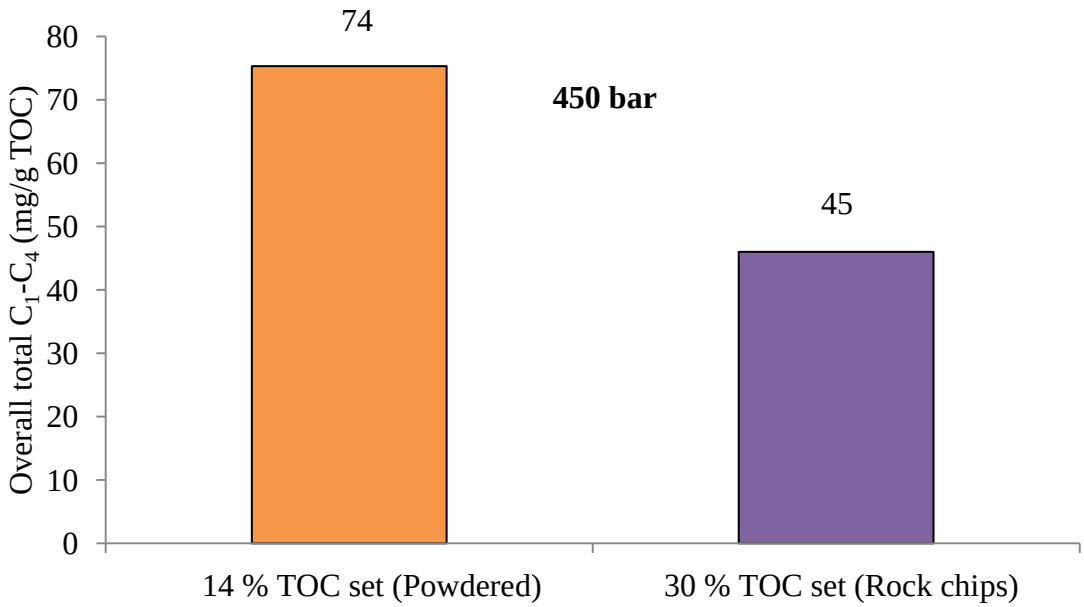

Fig. 5.21. Total gas yields for the 14 and 30 % TOC isolated partially matured source rock experiments at 420 °C for 24 h at 450 bar.

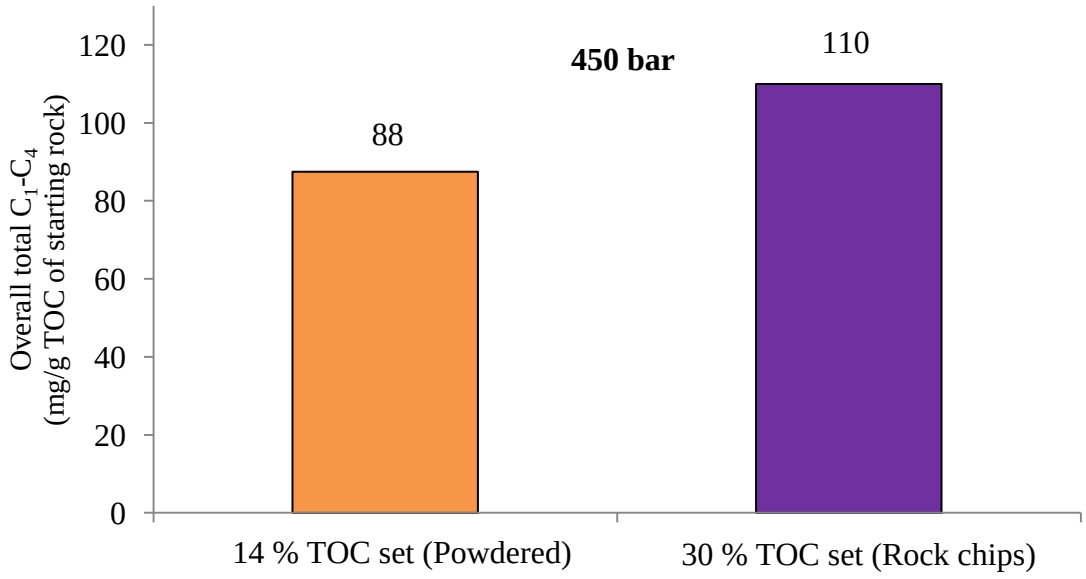

Fig. 5.22. Total gas yields for the 14 and 30 % TOC isolated bitumen cracking experiments at 420 °C for 24 h at 450 bar.

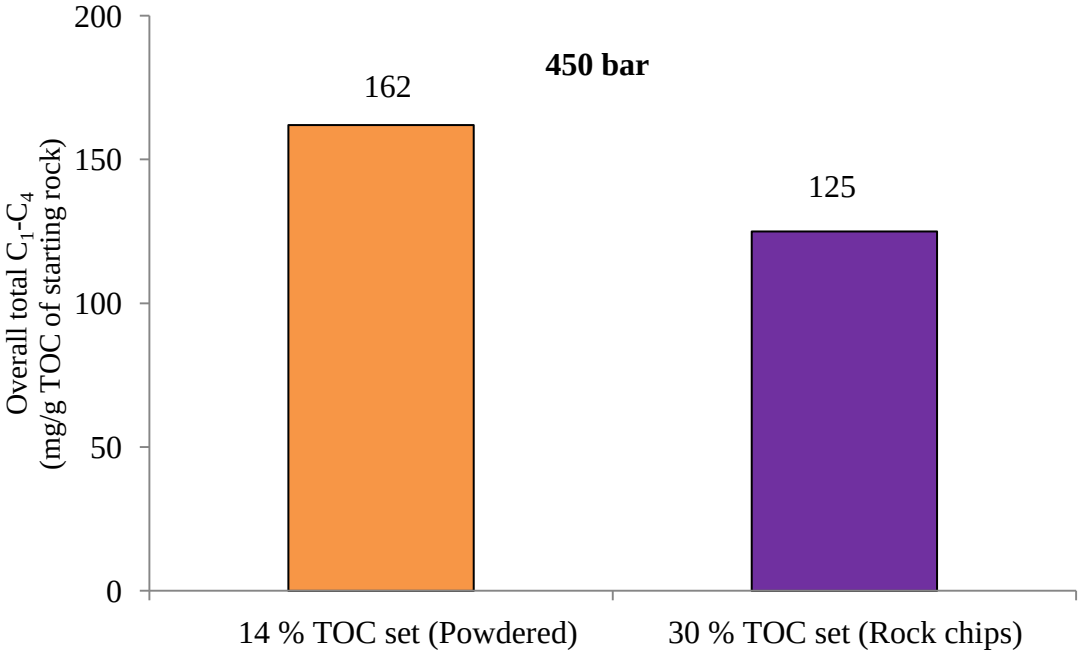

Fig. 5.23. Total gas yields for the 14 and 30 % TOC rock recombined mixture experiments at 420 °C for 24 h under 450 bar.

5.6.2. Bitumen plus oil yields.

Fig. 5.24 to 5.27 displays the bitumen plus oil yields from the whole rock, isolated partially matured source rock and bitumen and recombined mixture experiments, respectively, at 420 °C for 24 h. Similarly, the results from the partially matured source rock experiments (Fig. 5.25) will also be presented in mg of carbon of the starting partially matured source rock.

In the case of whole rock (Fig. 5.24) and partially matured source rock (Fig. 5.25) experiments, the bitumen plus oil yields were all higher from the 30 % TOC rock chip compared to the 14 % TOC powdered experiments. The higher bitumen plus oil yields is due to better expulsion of the bitumen plus oil from the rock chip samples compared to the powdered samples. In the case of the bitumen cracking experiments (Fig. 5.26), the slightly lower bitumen plus oil yield is expected due to lower amounts of starting bitumen from the 14 % TOC bitumen cracking experiments compared to the 30 % TOC bitumen cracking experiments. In the case of the recombined mixture experiments (Fig. 5.27), lower bitumen plus oil yields were obtained from the powdered experiments compared to the rock chip experiments due to the high amounts of unextractable bitumen adsorbed and retained in the powdered samples; whereas when using rock chips samples, only a small portion of the bitumen is adsorbed and retained onto the surface of the rock chips.

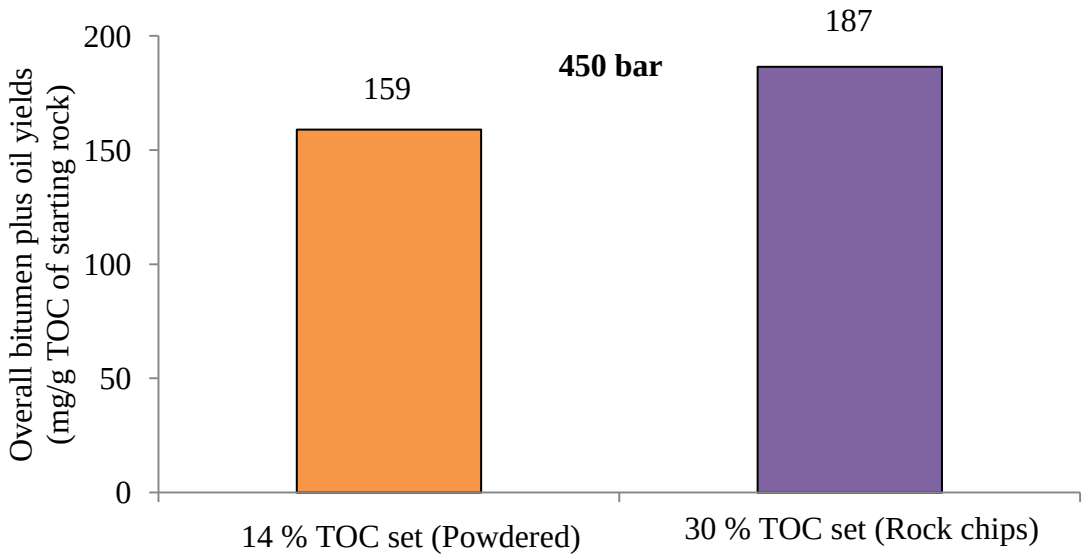

Fig. 5.24. Total bitumen plus oil yields for the 14 and 30 % TOC whole rock experiments at 420 °C for 24 h at 450 bar.

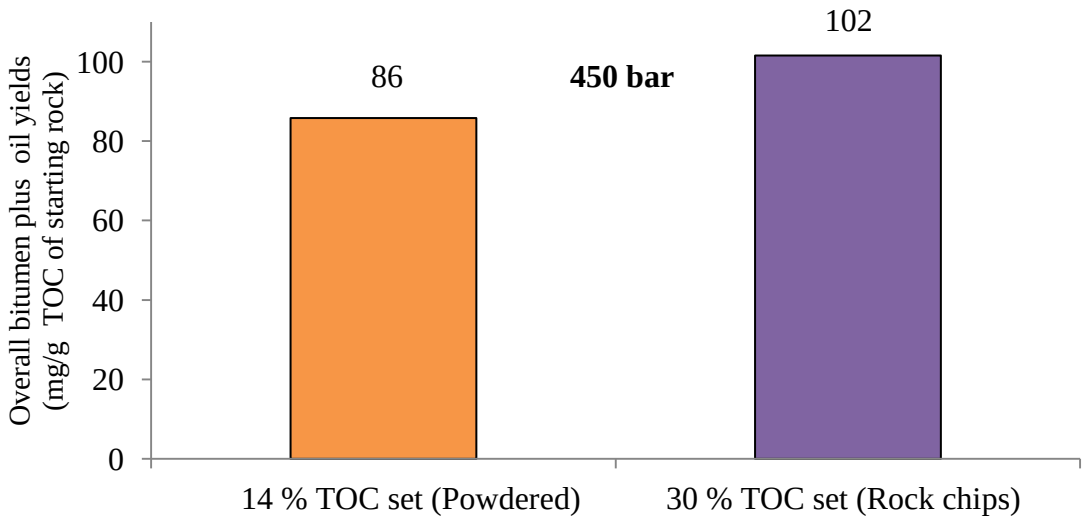

Fig. 5.25. Total bitumen plus oil yields (mg/g TOC) for the 14 and 30 % TOC isolated partially matured source rock experiments at 420 °C for 24 h at 450 bar.

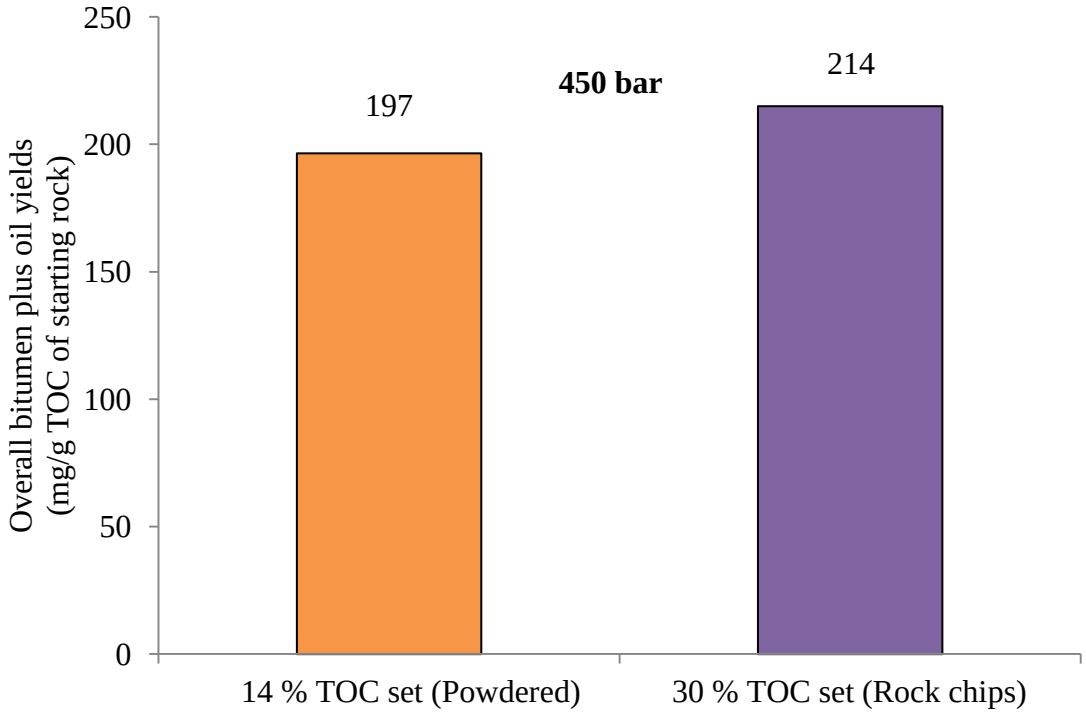

Fig. 5.26. Total bitumen plus oil yields for the 14 and 30 % TOC isolated bitumen cracking experiments at 420 °C for 24 h at 450 bar.

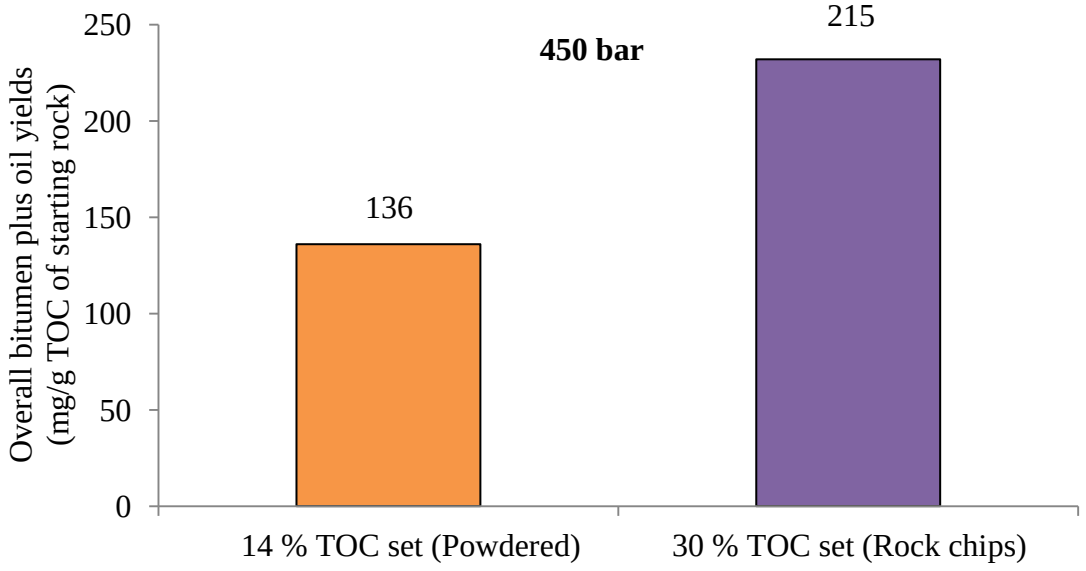

Fig. 5.27. Total bitumen plus oil yields for the 14 and 30 % TOC recombined mixture experiments at 420 °C for 24 h.

5.6.3. Coke yields.

Fig. 5.28 to 5.31 displays the coke yields from the whole rock, isolated partially matured source rock and bitumen and recombined mixture experiments, respectively at 420 °C for 24 h under 450 bar. Similar amounts of coke were generated from the whole rock (Fig. 5.28) and partially matured source rock (Fig. 5.29) experiments between the 14 and 30 % TOC source rocks. Fig. 5.30 shows that more coke was generated from the 30 % TOC set compared to the 14 % TOC set bitumen cracking experiments due to more bitumen present at the start of the 30 % TOC bitumen cracking experiments, which in turn cracks to form more coke. In the case of the recombined mixture experiments (Fig. 5.31), the higher coke yields from the 14 % TOC set is attributed to more bitumen being retained in the powdered samples as opposed to using the rock chips, where only a small portion of the bitumen is adsorbed on the surface of the rock chips. This is consistent with the lower bitumen plus oil yields generated from the 14 % TOC powdered experiments at 450 bar for 24 h (Fig. 5.27).

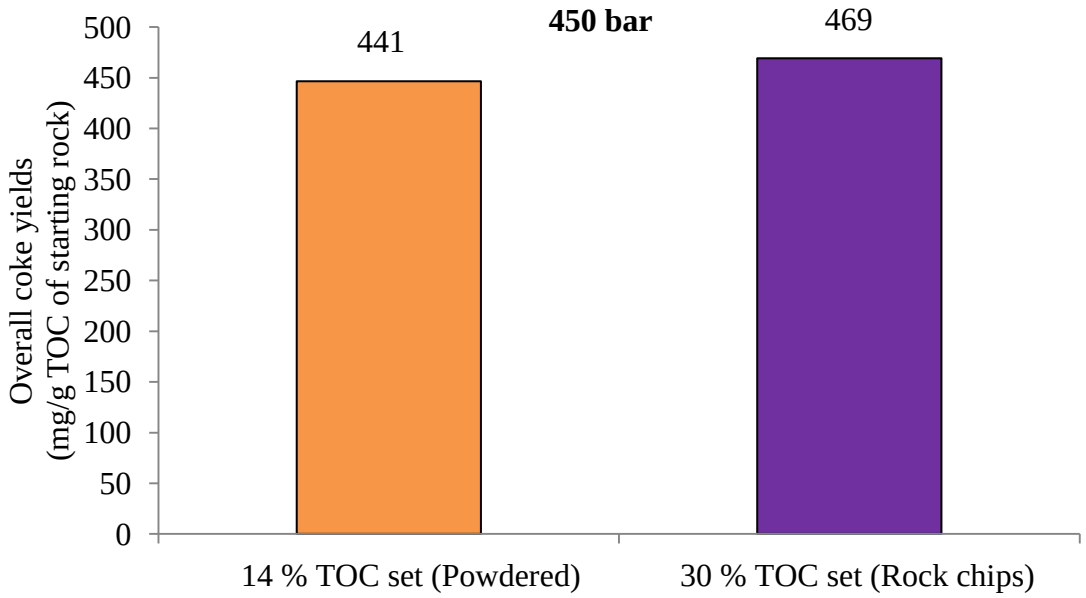

Fig. 5.28. Total coke yields for the 14 and 30 % TOC whole rock experiments at 420°C for 24 h at 450 bar.

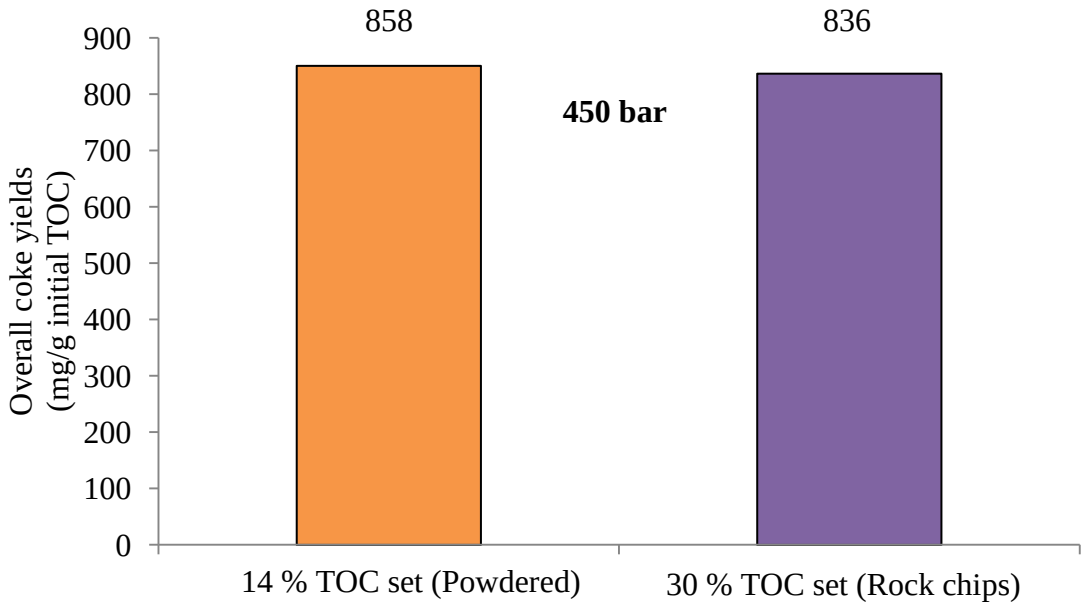

Fig. 5.29. Total coke yields (mg/g TOC) for the 14 and 30 % TOC isolated partially matured source rock experiments at 420 °C for 24 h at 450 bar.

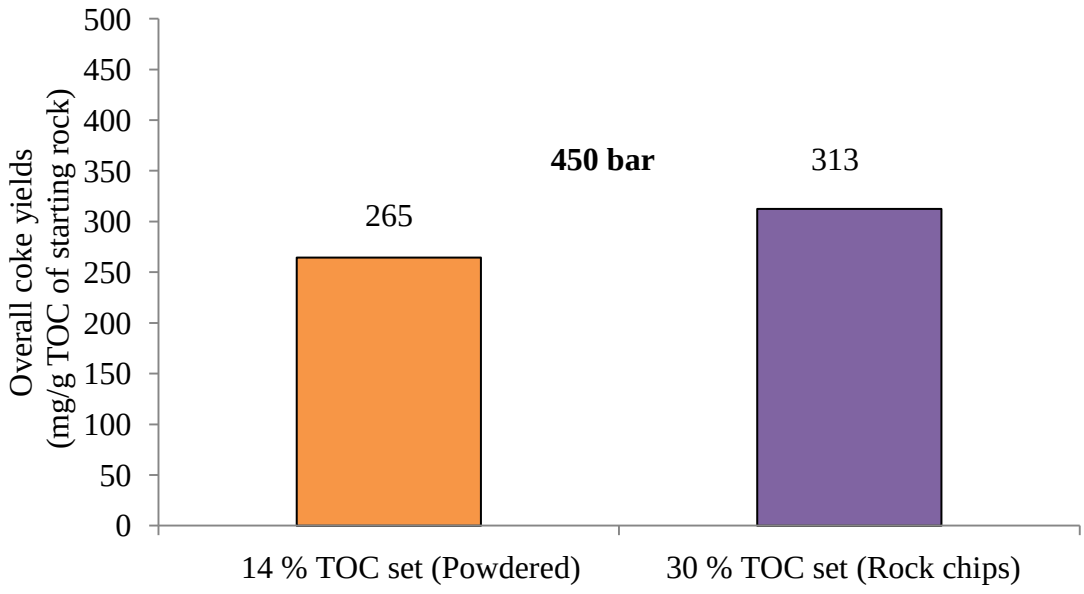

Fig. 5.30. Total coke yields for the 14 and 30 % TOC isolated bitumen cracking experiments at 420 °C for 24 h at 450 bar.

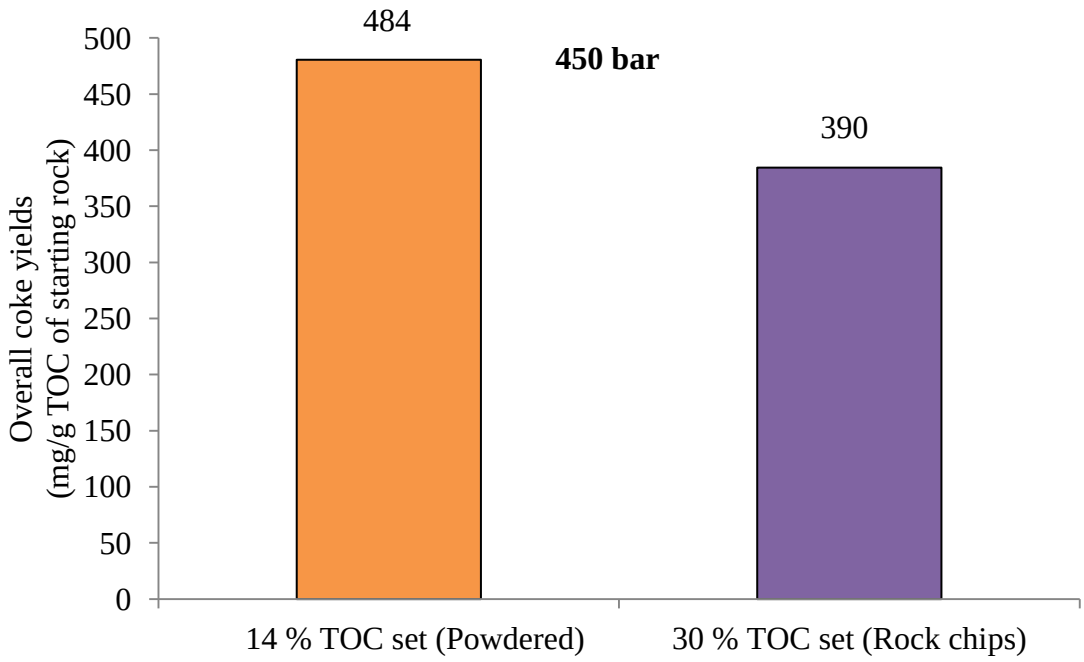

Fig. 5.31. Total coke yields for the 14 and 30 % TOC recombined mixtures experiments at 420 °C for 24 h at 450 bar.

Chapter 6: Discussion of results.

6.1. Effect of pressure on hydrocarbon generation and maturation.

The hydrocarbon (C_1-C_4) gas yields were always higher for all the experiments conducted at 350 °C under 180 bar pressure compared to 500 and 900 bar. The reduced gas yields observed going from 180 to 900 bar is due to pressure retarding gas generation from source rock and bitumen pyrolysis. This resulted in the bitumen being preserved from cracking, and more hydrocarbon generating potential being retained in the pyrolysed source rock. The formation of liquid hydrocarbons from whole rock samples was also retarded with increasing water pressure at 350 °C, which is consistent with the studies conducted by Price and Wenger, (1992) and Michels et al., (1995a & b). At 180 bar hydrous conditions at 350 °C a mixture of water and vapour exist in the reactor, and the available vapour space can accommodate more gas, hence the higher gas yield observed. At 500 and 900 bar water pressure, the vessel is entirely filled with liquid water with no vapour space available to accommodate the generated gas, and hence gas generation from source rock maturation and bitumen cracking is retarded. The reduction in gas yield observed under 500 and 900 bar conditions at 350 °C indicate that the reaction pathway occurring with an increase in water pressure resulted in the retardation of hydrocarbon generation, consistent with previous studies (Carr et al, 2009; Uguna et al., 2012a & b). In the case of the 14 % TOC source rocks at 350 °C for 24 h, the overall gas yields at 500 bar show that less gas was generated for both the partially matured source rock and bitumen pyrolysed individually (11 mg/g TOC), compared with the recombined mixtures of the partially matured source rock and bitumen (13 mg/g TOC), and the whole rock experiment (17 mg/g TOC). This trend shows that the pressure retardation effect is most significant for the partially matured source rock and bitumen when pyrolysed individually, becoming less significant for the recombined mixtures of partially matured source rock and bitumen, and least for the whole rock experiment. This also indicates that the pressure retardation effect is lower, but still

significant for experiments where the reactant phases (kerogen, bitumen, and mineral matter) that are in close contact potentially catalysing cracking reactions. In addition to the reduced gas yields, lower alkene gas yields were also generated with increasing water pressure at 350 °C. This is similar to the studies conducted by Domine (1989) on the pyrolysis of n-hexane using gold tubes that with increasing pressure, the light unsaturates production (C_2H_4, C_3H_6,) is all but stopped at high pressures, whereas light saturates yields decrease dramatically.

At 420 °C the gas yield was similar under low (310 bar) and high (450 bar) pressure conditions from the isolated fractions, recombined mixtures and whole rock experiments from the 14 % TOC source rocks, whereas similar gas yields were also obtained from the 25 % TOC source rocks at 500 and 900 bar for the whole rock and isolated fraction experiments. This is the effect of pressure becoming less significant as temperature becomes dominant over the 450 bar pressure applied, and not the high conversion achieved for gas generation at 24 h. This result is consistent with the previous studies performed by Uguna et al., (2012a & b), which shows that the effect of pressure was insignificant for gas generation between 6 and 24 h at 420 °C but significant at 350 °C in the pressure range of 450-900 bar. It is anticipated that the effect of pressure will still be significant if experiment was run at 350 °C for more than 24 h at 900 bar in order to achieve higher conversions. At 420 °C, the formation of liquid hydrocarbons was increased with increasing water pressure. This is similar to the studies conducted by Horsfield et al., (1992) on oil cracking, which shows that with increasing thermal stress high molecular weight aliphatic hydrocarbons undergo chain shortening and aromatic hydrocarbons increase in relative concentration. This could be the reason for the low aliphatic yields, and the increase in aromatic and total liquid hydrocarbon yields at 420 °C, where the water promotional effects and thermal stress are higher at 900 bar and 420 °C compared to all experiments at 350 °C.

Rock Eval pyrolysis data from the partially matured source rock shows that the trend in hydrocarbon gas yield going to high water pressure was similar to previous studies conducted on isolated kerogens (Michels et al., 1994), Kimmeridge Clay source rock

(Carr et al, 2009; Uguna et al., 2012a) and coals (Uguna et al., 2012b), where the reduction in gas and bitumen yields at high water pressure resulted in the concurrent increase in residual rock S_2 and HI from Rock Eval pyrolysis. However, in the case of the partially matured source rock experiments conducted with the 25 % TOC source rocks, the Rock Eval pyrolysis data at 420 °C shows a reversal trend HI and $S_{2,}$ which is in contrast to those observed at 350 °C. The decrease of HI registered between 310 and 900 bar is poorly understood for now. However, a similar trend is also observed by Blanc and Connan (1992), where their pyrolysis studies of Paris Basin Toarcian source rock with gold sealed tubes at 330 °C for 6 h to 14 days show a similar decrease in HI when pressure was increased from 550 bar to 1000 bar.

In terms of pyrobitumen formation, the amount of pyrobitumen formed from the whole rock, isolated fractions and recombined mixtures were retarded with the increase in pressure at both 350 and 420 °C, apart from the isolated bitumen cracking experiments conducted at 420 °C with the 25 % TOC bitumen, which shows that when pressure was increased from 310 to 900 bar, the amount of coke formed was also increased from 403 to 469 mg/g TOC. This is in contrast to what was observed from the coke yield trends, where an increase in water pressure at 420 °C results in a decrease in residual TOC yield and hence pyrobitumen formation. Hill et al., (1996) suggest that pyrobitumen generation occurs by aromatization and ring condensation reactions. Their studies on oil cracking show that at 400 °C, pyrobitumen yield decreases with increasing pressure from 90 to 483 bar, which they attribute the decrease in yield between 90 and 483 bar to the high activation energy for activated complex formation which favours recombination reactions over chain propagating reactions. Pyrobitumen yield peaks at 690 bar and then steadily decreases from 690 to 2000 bar. This mirrors the coke yield trends observed from the isolated bitumen cracking experiments from the 25 % TOC bitumen. Overall, the coke yields are expected to decrease if experiments were conducted at pressures above 900 bar at 420 °C.

Although the results indicate that the 14 and 25 % TOC KCF whole rock, isolated fractions and recombined mixtures behave similarly due to parallel trends in terms of

hydrocarbon generation and source rock maturation (VR values) under the same experimental conditions, the reduction in coke yield with increasing water pressure was not so significant from the 14 % TOC whole rock and all isolated partially matured source rock experiments compared to the 25 % TOC whole rock at 350 °C, where as a noticeable decrease was observed from the 25 % TOC whole rock. This can be explained by Braun and Burnham, (1990) where they state that for the highest organic content (in this case the 25 % and possibly the 30 % TOC whole rocks), little additional oil degradation occurs resulting in more extractable liquid products. Conversely, for the lowest organic content (in this case the 14 % TOC whole rocks and all isolated partially matured source rock experiments), much of the remaining oil is cracked to form pyrobitumen or coke. Extreme cracking occurs for the very low organic material, because the bulk volume generation is insufficient to expel what little oil was generated. Hence, the extreme cracking of these low residual TOC source rocks (especially for the partially matured source rock where the initial TOC is very low) might counter act the pressure retardation effects on pyrobitumen formation.

The VR values follow the same trend as the gas yield at 350 °C, decreasing by 0.6 and 0.5 % Ro from the whole rock and partially matured source rock in isolation experiments, respectively, going from 180 to 500 bar. An increase in temperature to 420 °C resulted in an increase of VR as expected, with VR reaching a maximum of 2.0 % Ro at 310 bar before decreasing to 1.7 % Ro at 450 bar from the whole rock experiment. The partially matured source rock isolation experiment also shows a reduced VR of 0.2 % Ro going from 310 to 450 bar. The reduction in VR observed at 420 °C under high pressure conditions is in contrast to gas generation which was not affected by pressure. The reduced VR observed under high water pressure conditions at both 350 and 420 °C indicate that water pressure has a retardation effect on source rock maturation, which is consistent with the previous studies by Uguna et al., (2012a & b). The reduction in VR at high water pressure at 350 °C is due to a possible combination of the retention of volatiles in the residual rock caused by pressure retardation on hydrocarbon generation, and due to pressure reducing the rate of aromatisation reactions which in turn reduces residual rock aromaticity (Carr, 1999). Retention of volatiles in source rocks or kerogen

prevents the reorganisation of the structure required to produce the polycyclic aromatic molecules that account for higher vitrinite reflectance (Carr, 1999). However, at 420 °C the reduced VR at 450/500 and 900 bar pressure might be due to lower residual rock aromaticity caused by pressure reducing the rate of aromatisation reactions, as the high water pressure did not retard hydrocarbon gas generation which leads to retention of volatiles.

Overall, the results clearly shows that when bitumen is in intimate contact with the kerogen, hydrocarbon generating reactions are likely to be facilitated that have a weak pressure dependency. These reactions will potentially produce more gas offsetting the effect of pressure in retarding bitumen cracking. However, further work is required to ascertain the extent of mineral matter catalysis from clays on bitumen cracking in high water pressure since this could partly be responsible for the reduced gas yields from the bitumen in isolation.

6.2. Effect of reactant phase on hydrocarbon generation and maturation.

The C_1-C_4 gas yields were always higher for all whole rock experiments when compared with those obtained from the experiments on isolated fractions (partially matured source rock and bitumen in isolation) and the recombined mixtures at 350 and 420 °C under the same pressure conditions. The gas yields obtained from the recombined partially matured source rock and bitumen mixtures were intermediate between those from the whole rock and the isolated fractions. The higher gas yields observed from the whole rock experiments is due to source rock, bitumen and mineral matter being in intimate contact, which facilitated hydrocarbon gas generation with the possibility of mineral matter catalysing the reactions, and bitumen promoting hydrocarbon generating reactions. This might indicate that the reactant phase is important during hydrocarbon gas generation. Pressure retardation effect is most significant for the isolated fractions, becoming less significant for the recombined mixtures, and least for the whole rock experiment (where the reactant phases such as kerogen, bitumen, and mineral matter are in close contact). This also indicates that the pressure retardation effect is lower, but still significant for whole rock experiments.

Higher gas yields were also generated from the recombined mixture experiments (149 mg/g TOC) compared to the isolated bitumen in the presence of montmorillonite (116 mg/g TOC) at 420 °C under 450 bar. This might indicate that other than the reactant phase, the intimate interaction between kerogen and minerals might also facilitate hydrocarbon gas generation. Most pyrolysis studies on minerals usually require the kerogen to be isolated and demineralised from the source rock (Tannenbaum et al., 1986; Huizinga et al., 1987a & b). However, Pan et al., (2008) suggested that the organic matter in marine sediments is closely associated with the mineral phase because there is a direct proportionality between organic matter concentration and sediment surface area. When kerogen is isolated from source rocks by dissolving minerals, the natural association between the two phases is also destroyed (Mayer, 1994a & b; Keil et al., 1994). Furthermore, the three dimensional structure of kerogen undergoes some change during the removal of the mineral matrix, liberating extractable trapped compounds (Vandenbroucke and Largeau, 2007). This might explain the higher gas yields generated

from the recombined mixture experiments (where the natural association between the reactant phases are retained) compared to the isolated bitumen in the presence of montmorillonite. Other than the presence of mineral matter, Larsen and Hu (2006) also proposed that pyrite (which comprises more than 40 wt % in source rocks) is able to catalyse hydrous pyrolysis. In our study, the source rock was not demineralised or treated with $CrCl_2$ to remove pyrite. The higher gas yields generated from the recombined mixture experiments might also be from the additional influence of pyrite.

In addition to the higher gas yields, lower bitumen plus oil yields and higher coke yields were generated from the isolated bitumen experiments in the presence of montmorillonite powder, compared to the recombined mixtures (where the bitumen is adsorbed to the partially matured source rock). Montmorillonite clay minerals have been reported to be the most active in "retaining" the heaviest hydrocarbon compounds and in promoting their coking as the temperature rises (Espitalié et al., 1980; Horsfield and Douglas, 1980; Tannenbaum et al., 1986; Huizinga et al., 1987a & b). The retained heavier fractions in the bitumen (> $n$$C_{15}$) on the minerals allows secondary fragmentation of these heavier compounds into smaller molecules or hydrocarbon gas. Since the Kimmeridge Clay Formation source rock commonly comprises of clay minerals (20-65 %) in the form of illite and kaolinite with minor amounts of chlorite and smectite (Scotchman, 1987 & 1990; Morgans Bell et al., 2001), where the adsorption strength of these minerals towards the bitumen is much less compared to montmorillonite (Espitalié et al., 1980; Horsfield and Douglas, 1980; Tannenbaum et al., 1986; Huizinga et al., 1987a & b), this explains why more bitumen plus oil yields and less coke were generated from the recombined mixtures experiments compared to the isolated bitumen experiments in the presence of montmorillonite.

The C_1-C_4 gas yields were also higher from the isolated bitumen cracking experiments in the presence of the powdered montmorillonite under both anhydrous (25 bar) and high water pressure (450 bar) at 420 °C compared to the same experiments without the powdered montmorillonite. Although the most apparent increase in gas yields was under anhydrous conditions, a noticeable increase in gas yields was also observed under high

water pressure conditions as well. It has been reported extensively that under hydrous conditions, the hydrocarbon gas generation were not significant even in the presence of montmorillonite, due to the catalytic effects of the clay minerals being diminished as water competes for the reaction sites on the clays (Espitalié et al., 1980; Horsfield and Douglas, 1980; Tannenbaum et al., 1986; Huizinga et al., 1987a & b). However, as previously discussed in Section 2.11, there are some evidences of catalytic effects under hydrous conditions reported by several authors (Espitalié et al., 1984; Eglinton et al., 1986), although not to a high degree as those performed under anhydrous conditions. Despite not many studies on the effect of clay minerals in the presence of bitumen, Tannenbaum and Kaplan (1985) have stated that the catalysis effect of clay minerals was found to be stronger with bitumen than for kerogens. This might cause the slight increase in gas yields when bitumen was cracked in the presence of the montmorillonite and in the presence of water under high pressure conditions, compared to the experiments without montmorillonite.

The thermal maturity of the bitumen plus oil was also observed to be slightly higher from the experiments conducted with whole rock, partially matured source rock and recombine mixture samples compared to bitumen in isolation. The C_{29} and C_{30} hopane ratios always show a higher maturity from the bitumen plus oil generated from the partially matured source rock, recombined mixtures and whole rock experiments compared to the isolated bitumen experiments. This implies that the bitumen cracking in the presence of source rocks facilitate stronger isomerisation of the C_{29} and C_{30} hopanes compared to when bitumen was pyrolysed individually. The highest isomerisation and maturity obtained from the partially matured source rock might be due to the high kerogen to residual bitumen ratio from the partially matured source rock experiments. Pan et al., (2012) have shown in their studies that the presence of coals accelerates oil cracking into hydrocarbon gases, which might also be the reason for the stronger isomerisation experienced by the bitumen plus oil in the presence of the partially matured source rock or whole rock.

As already described, the VR of the source rock residues are higher from the whole rock experiments compared to the isolated source rock maturation experiments for all the experimental conditions. Although it is suggested by Carr, (2000) that the presence of bitumen and oil are known to suppress vitrinite reflectance, the higher VR observed for whole rock experiments might indicate otherwise. This might be due to the presence of bitumen facilitating free radical transfer reactions resulting in aromatisation reactions occurring to a greater extent in the whole rock experiments. Aromatisation reactions increase the carbon aromaticity of the source rock residues, which in turn increases the VR (Carr, 1999). The lower VR shown by the source rock maturation experiments in isolation is consistent with the observed overall lower gas yield.

The effect of sample size also has an influence on hydrocarbon gas as more hydrocarbon gas was generated from the 14 % TOC source rocks due to the larger surface area of the powdered KCF sample facilitating gas generation. This is most apparent when comparing the gas yields generated from the recombined mixture experiments conducted with the powdered and rock chip KCF samples at 420 °C at 450 bar. Despite having more initial bitumen (1.0 g) adsorbed on to the partially matured rock chips compared to the lesser amounts of initial bitumen (0.8 g) adsorbed onto the powdered partially matured source rock, higher gas yields were generated from the powdered samples (162 mg/g TOC) compared to using rock chips (125 mg/g TOC). This implies that interactions between reactant phases are more pronounced when using powdered samples compared to using rock chips, where the interactions between the reactant phases slightly hindered.

Clearly, much more data is needed before these aspects of interaction between reactant phases including the effect of high water pressure during the geological thermal evolution of organic matter are understood in a satisfactory manner. However, the results obtained in this study demonstrates that the interplay of inherent mineral matter, reactant phase, source rock/kerogen, bitumen and pressure are key factors in determining the extent of hydrocarbon generation and source rock maturation in geological basins.

Chapter 7: Conclusions and future work

- For the type II Kimmeridge Clay Formation source rock, the hydrocarbon gas yields were higher for whole rock compared to the partially matured source rock and bitumen in isolation. The gas yields were intermediate for mixtures of the partially matured source rock and bitumen. The VR were also higher from the whole rock experiments in comparison to partially matured source rock when pyrolysed in isolation. The biomarker ratios also shows a more mature bitumen plus oil was generated from experiments in the presence of the source rocks compared to bitumen pyrolysed individually. This indicates that hydrocarbon gas generation, bitumen plus oil and source rock maturation is facilitated by interactions between the source rock, bitumen and the associated mineral matter.

- High water pressure was found to retard gas generation at 350 °C but not at 420 °C due to temperature being dominant over pressure at the higher temperature. However, pressure retarded source rock maturation in both the partially matured source rock and whole rock experiments at 350 and 420 °C. The retardation effect of pressure on hydrocarbon gas generation was much greater from the partially matured source rock and bitumen pyrolysed in isolation compared to the partially matured source rock and bitumen mixtures and the whole rock experiments. This implies that when bitumen and kerogen are in intimate contact, hydrocarbon generating reactions are facilitated, and these will potentially produce more gas offsetting the effect of pressure in retarding oil cracking.

- The results obtained in this study demonstrated that the reactant phase in terms of the source rock/kerogen, mineral matter and bitumen being in intimate contact is important for promoting the reactions responsible for source rock maturation and hydrocarbon gas generation. As such, the intimate contact between the reactant phases (kerogen, bitumen and mineral matter) and pressure are both important factors in determining the rate of reaction during hydrocarbon gas generation and source rock maturation in geological basins.

- Future work will include isolated bitumen cracking experiments conducted with the actual Kimmeridge clay minerals (such as illite, kaolinite, chlorite and smectite), other clay minerals (montmorillonite) or transition metals (pyrite) at 350 and 420 °C for 24 h under hydrous and high water pressure conditions. This is to determine the effect of different minerals and transition metals on hydrocarbon generation during bitumen cracking under the influence of increasing water pressures.

- Recombined mixture experiments will be conducted with different partially matured source rock to bitumen ratios, and different coal to bitumen ratios. This study will be conducted in order to ascertain the minimum amount of partially matured source rock or coal required to catalyse gas generation from the bitumen cracking in the recombined mixtures before retardation in gas generation is observed (Pan et al., 2012).

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